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Baseline Scotland: groundwater chemistry of southern Scotland

Groundwater Resources Programme

Open Report OR/08/62

BRITISH GEOLOGICAL SURVEY

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Moffat Well: a mineralised spring in southern Scotland.

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Foreword

In its natural state, groundwater is generally of excellent quality and an essential natural resource for Scotland. Groundwater directly accounts for at least 7% of public water supply, as well as sustaining river flows and providing water for some 30 000 private supplies. However, the natural quality of groundwater in our aquifers is continually being modified by the influence of man. This occurs due to direct and indirect anthropogenic inputs and to groundwater abstraction. Therefore, a thorough knowledge of the quantity and quality of groundwater in our aquifers, including an understanding of the processes that affect groundwater, is essential for effective management of this valuable resource.

Baseline Scotland, jointly conceived and funded by the British Geological Survey (BGS) and the Scottish Environment Protection Agency (SEPA), seeks to improve data availability and general understanding of the chemistry of Scotland's groundwater. The primary aim of the project is to provide core hydrogeological data and interpretation to help in the implementation of the Water Framework Directive. An overview of groundwater chemistry data for Scotland during the inception phase (MacDonald and Ó Dochartaigh 2005) highlighted the paucity of reliable data for natural substances that occur in groundwater. Good-quality data that do exist are available for only small areas, such as the Dumfries Permian aquifer, but the Water Framework Directive requires an understanding of background groundwater chemistry across a much broader area.

The aims of *Baseline Scotland* are:

1. To characterise the ranges in natural background groundwater quality in the main aquifer types in Scotland, by carrying out groundwater sampling surveys that as far as possible incorporate representative areas of each aquifer, allowing extrapolation of the interpreted results to the remaining parts of each aquifer; and
2. To provide a scientific foundation to underpin Scottish, UK and European water quality guideline policy, notably the Water Framework Directive, with an emphasis on the protection and sustainable development of high quality groundwater.

The project runs from 2005 to 2010, during which time systematic surveys will be undertaken across the different aquifers of Scotland. As we move forward, Scotland will be in a much better position to develop and manage its groundwater resources.

Alan MacDonald BGS

Vincent Fitzsimons SEPA

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Summary

This report describes the baseline groundwater chemistry of bedrock aquifers in southern Scotland, from the Scotland-England border to the Southern Upland Fault, with the exception of the highly productive Permian aquifers, which are treated separately. Four main aquifer groups are considered: sedimentary and metasedimentary rocks of both Ordovician and Silurian age; Devonian sedimentary rocks; and Carboniferous sedimentary rocks. There are also small outcrops of igneous rocks, mainly granite and lavas. There are at least 1000 individual groundwater sources in the study area, with the vast majority of abstractions being for private domestic or small farm use. These are concentrated in the main settled areas: the coastal fringes and major valleys.

A total of 47 new samples were collected for analysis from the Ordovician and Silurian (Lower Palaeozoic), Devonian, Carboniferous and igneous aquifers in the study area during this project: 25 from the Borders between September and November 2005, and 22 from Dumfries and Galloway in July 2006. These were augmented with a further 31 samples collected during separate BGS projects since 2002. Sources were chosen to be representative of groundwater in the area, and sources that were very poorly constructed were avoided.

The hydrochemistry data and information on groundwater residence times can help give an insight into groundwater flow in aquifers across southern Scotland. In all the aquifers sampled, groundwater flow is largely through fractures and is well mixed in the top 50 metres or so. There is no evidence of palaeowater in the area, and all samples recorded some proportion of water less than 50 years old. However, groundwater can be resident for several decades, even in the more fractured, less permeable Lower Palaeozoic aquifers.

Overview of groundwater chemistry in southern Scotland

Most of the groundwater pH values in the region are in the near-neutral range (6.5–8.5). Groundwaters from Ordovician and Silurian rocks tend to have a slightly lower pH than those from Devonian sandstones and Carboniferous sandstones and limestones. Groundwaters from igneous rocks and mineralised Lower Palaeozoic strata are more acidic, with occasional pH values below 6.5. Similar patterns are observed in bicarbonate alkalinity, with HCO_3 in the range 100–250 mg/l for Ordovician and Silurian groundwaters, 200–320 mg/l for Devonian and Carboniferous groundwaters, and <100 mg HCO_3/l for igneous and mineralised Lower Palaeozoic groundwaters. Cl and SO_4 concentrations are generally low and reflect inputs from rainfall, with the exception of Carboniferous groundwaters which tend to have highest concentrations of Cl and SO_4, possibly reflecting the influence of connate water and sulphide mineralisation within interbedded mudstone.

Concentrations of the major cations reflect a combination of rainfall input, mineral weathering, and anthropogenic inputs derived from the use of fertilisers and liming (or from other sources of pollution). Most notable is an enrichment of K (5–10 mg/l) in groundwaters from Carboniferous sedimentary rocks, probably resulting from feldspar weathering. Ca concentrations broadly reflect the distribution of calcite in aquifer rocks. Groundwater from Ordovician, Silurian and mineralised strata and igneous aquifers are undersaturated with respect to calcite, as would be expected from their non-carbonate mineralogy. Groundwater from the Devonian and Carboniferous strata are generally saturated or supersaturated with respect to calcite, indicating the presence of calcite either as a major (Carboniferous limestone) or minor (calcite cement in Devonian sandstones) component. There is a good positive correlation between Mg and Ca concentrations, especially for low Ca concentrations (<80 mg/l).

Most of the groundwaters in the study area are oxidising, with dissolved oxygen concentrations in the range 1–7 mg/l and a redox potential (Eh) greater than 300 mV. However, the mineralised springs are reducing, with sulphate reduction indicated at St Ronan's Well. Groundwaters from Carboniferous strata in general tend to be slightly less oxidising than those from other aquifers. Apart from these incidences, however, the groundwater redox status does not appear to vary strongly with geology.

Nitrate and phosphorus

In each of the aquifer groups the median concentration of nitrate in groundwater is less than 5 mg/l NO_3-N; in each group except the Ordovician aquifer, at least 90% of samples show nitrate concentrations that are less than the drinking water limit of 11.3 mg/l NO_3-N (50 mg/l NO_3) (in Ordovician aquifers the 90th percentile for NO_3-N is 20.1 mg/l). Concentrations are related to land use, with groundwaters beneath agricultural land showing higher concentrations than beneath non-agricultural land. The land use classification showing the highest median NO_3 concentration was land used for rearing 'dairy, pigs and poultry', as found in other parts of Scotland (MacDonald et al. 2005).

Elevated nitrate concentrations (> 5 mg/l NO_3-N) are found outwith the current designated Nitrate Vulnerable Zones (NVZs). The most noticeable are in the west of the study area in Galloway, where high concentrations are associated with improved pasture, and in particular dairy farming. Residence time indicators were used to examine nitrate concentrations further, and indicate a tendency towards higher nitrate where there is a higher fraction of modern water present. While the correlation is not particularly strong, there is a trend between sources on semi-natural land (older groundwaters) and some of the arable and improved-pasture sites (younger/higher proportion of recent recharge).

Phosphorus in groundwater can be an important influence on surface water eutrophication if present in baseflow to streams and rivers. Median P concentrations for the aquifer units in southern Scotland tend to fall in the range 30-70 µg/l-P. Phosphate concentrations do not show any strong relationship with land use, illustrating the complexity of P geochemistry, and the important role that soil geochemistry plays in the mobilisation of P into groundwater.

Mineralised springs

The three mineralised springs sampled show very different chemical compositions. St Ronan's Sulphur Spring is the most mineralised, with high concentrations of Na, Ca and Cl, and a wide range of trace constituents, notably Ba, Br, Li, I, Rb and Mn. Hartfell Spa is known as a chalybeate ('iron-rich') spring, and is strongly acidic with high concentrations of Fe, Al, Si, Mn and SO_4, and a wide variety of trace metals, including Ni, Co, Cu, Y, Tl, Be, Sc, Zn, Sn and many of the rare earth elements. The nearby Moffat Well is slightly alkaline, probably reducing, and rich in Na and Cl. It contains high concentrations of Ba, Ge, Li, Br and B. It was one of only two groundwaters in the study to show detectable Au, and had the highest observed Au concentration (0.41 µg/l).

Baseline

An estimate of the baseline groundwater chemistry conditions for southern Scotland is given by the statistical summaries of data collected during this survey, with the exception of NO_3-N and P where the influence of anthropogenic activity is likely to have distorted baseline conditions throughout many of the aquifers. Baseline conditions are likely to be represented by data between the 10th and 90th percentiles. To complement this approach, ten analyses of groundwater samples collected from high quality groundwater sources were chosen, which are unlikely to have been impacted by any agricultural contamination, and which represent the general groundwater conditions in the Silurian, Ordovician, Devonian and Carboniferous aquifers.

1 Introduction

This report describes the baseline groundwater chemistry of bedrock aquifers in southern Scotland, from the Scotland-England border to the Southern Upland Fault (Figure 1). This area encompasses virtually all of the counties of Borders and Dumfries and Galloway. The highly productive Permian aquifers in the area are not included, as they are dealt with elsewhere (Robins and Ball 2006, MacDonald et al. 2003).

Groundwater is an important resource in southern Scotland. Although comprehensive groundwater abstraction records do not exist, there are at least 1000 individual groundwater sources in the study area. These are concentrated in the main settled areas: the coastal fringes and major valleys. The vast majority of abstractions are for private domestic or small farm use. There are also a number of public water supply boreholes, largely drilled into superficial deposits. Other groundwater abstractors are mineral water companies and industries, particularly in the textile towns such as Galashiels and Selkirk, and dairies or creameries, particularly in Dumfries and Galloway. In the last few years there has been ongoing drilling of new abstraction boreholes, mainly for private domestic use, either to replace existing traditional springs or wells, or to supply new builds.

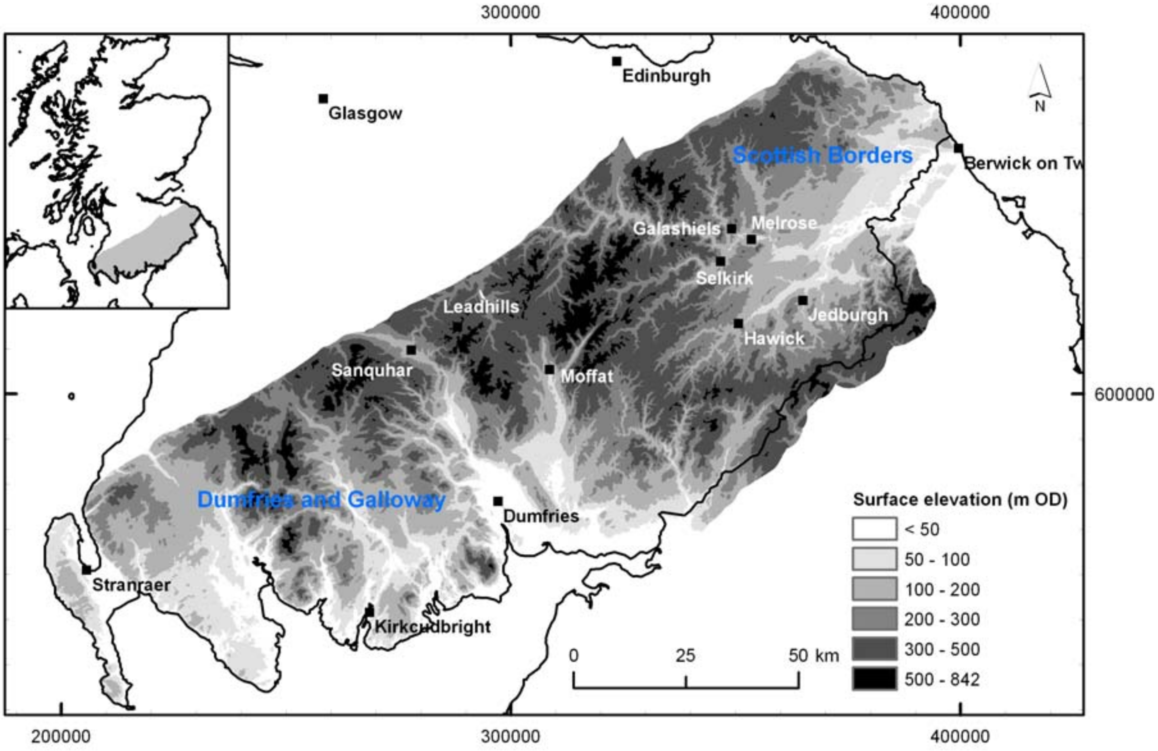

Figure 1 The area of study in southern Scotland, showing land surface elevation and locations mentioned in the text.

2 Background

In order to understand the chemistry of the groundwater in the area, we need to understand the environmental context. Knowledge of the geological, geochemical and hydrogeological properties is needed to provide a physical framework for the system. It is also useful to know the chemistry of rainfall in order to define the initial composition of groundwater recharge.

2.1 LAND USE

Much of the study area is upland, dominated by the Southern Uplands. Hill and high moorland are common (Figure 1). Sheep farming and commercial forestry comprise the majority of land use in these areas. Arable land and improved pasture, dominates much of the lowland parts of the study area. Dairy farming is common in the southwest: Dumfries and Galloway is one of the main dairy areas in Scotland, and a number of creameries are found in the major towns, including Stranraer and Kirkcudbright. Much of the east, along the Berwickshire coast, and smaller areas of the southwest around Dumfries and Stranraer, consist of low-lying, fertile land, including some of the most important arable agricultural land in Scotland (Figure 2). Much of this arable land lies within one of Scotland's four nitrate vulnerable zones. Figure 3 and Figure 4 show typical examples of the land use.

Many of the major settlements in the Borders, including Galashiels, Hawick, Selkirk, Melrose and Jedburgh, are dominated by the textiles industry. Further west, mining was formerly an important industry, both for coal at Sanquhar and for lead and other ore in the Leadhills area.

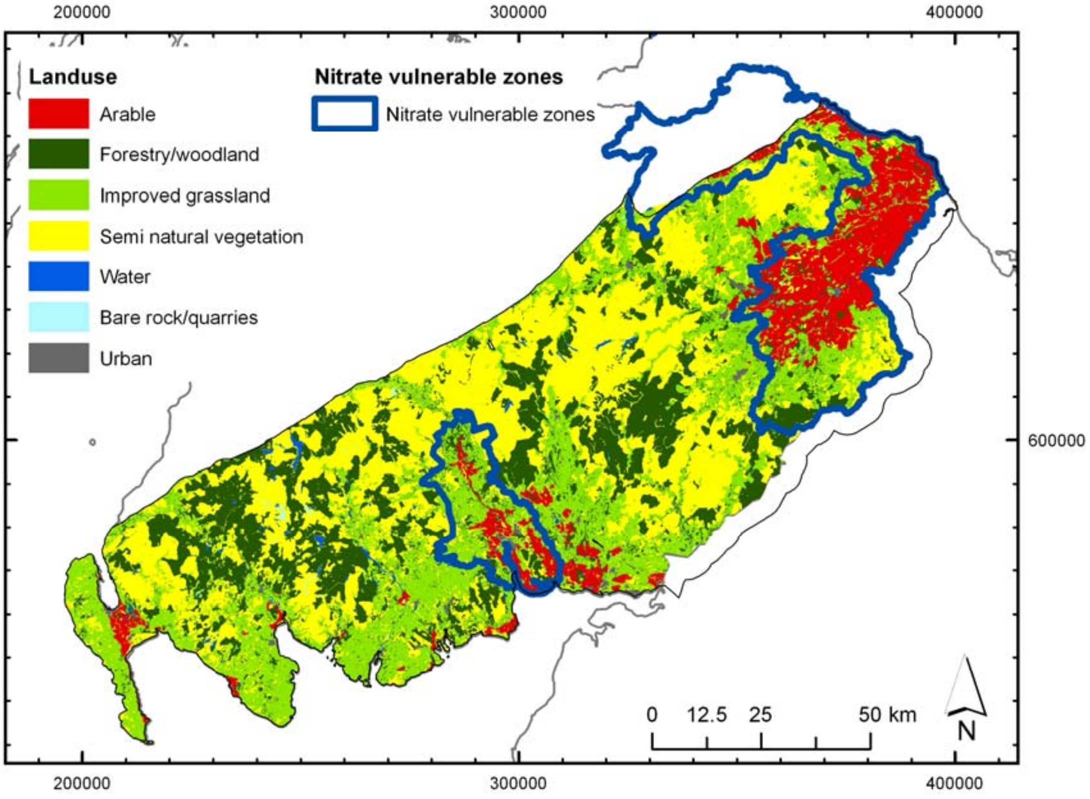

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Figure 2 Generalised land use and nitrate vulnerable zones in southern Scotland.

Figure 3 Cultivated valley in southern Scotland, with a mixture of arable and grazing land.

Figure 4 Upland area of southern Scotland: typically mixed grazing by sheep and cattle with some forestry.

2.2 BEDROCK GEOLOGY

2.2.1 Introduction

The bedrock geology of southern Scotland is shown in Figure 5**.** The study area is within the Southern Uplands terrane, which formed at the Laurentian continental margin during late Ordovician to mid Silurian subduction of the Iapetus Ocean. The terrane is bounded to the north by the Southern Upland Fault. The rocks in the Southern Uplands are dominated by Ordovician and Silurian strata, which comprise mainly turbidite greywackes and siltstones, which have been affected by large-scale structural forces. Carboniferous sedimentary rocks are important along the southeast boundary of the study area, and Devonian sandstones occur in the central-eastern parts of the area. Permian and Triassic sandstones occur in the southwest, although these aquifers did not form part of the current study. A summary of the geology is given here; further details can be found in the referenced studies.

2.2.2 Lower Palaeozoic

The Lower Palaeozoic rocks of the Southern Uplands represent a basin filled dominantly with marine turbiditic sandstones and siltstones, and minor conglomerates (greywackes), with a very small proportion of marine lavas, volcaniclastics, mudstones and cherts. The sediments were laid down over a period of about 75 million years from the mid Arenig (495 Ma) to the late Wenlock epoch (420 Ma). The rocks are divided into structural tracts by major southwest-northeast strike-parallel faults, and in general become younger southwards.

The Ordovician rocks of the Southern Uplands are divided (in order of decreasing age) into the Crawford Group, the Moffat Shale Group and the Leadhills Supergroup. The Silurian rocks are divided (also in order of decreasing age) into the various units of the Gala Group, the Hawick Group, the Riccarton Group, the Reston Group and the Lanark Group. These are described below based on information from Floyd (2001) and Oliver et al. (2002).

The oldest of the Lower Palaeozoic rocks in the study area belong to the **Crawford Group**, of Arenig to Llanvirn age. These are found as narrow outliers within younger rocks across the northern part of the study area. They include mudstones, cherts and igneous rocks, particularly pillow basalts.

The **Moffat Shale Group** ranges in age from Caradoc (Upper Ordovician) to Lower Silurian. It comprises a condensed graptolitic, carbonaceous shale, thought to be largely of pelagic, open-ocean origin, with thin interbedded cherts, and also meta-bentonite bands that represent fossil volcanic ash falls. The group is typically seen as elongated NE-SW trending inliers among younger rocks, interpreted as slivers of oceanic sediment caught up in hanging wall anticlines on fault walls. The age of these inliers decreases from north to south. They are most common within the Leadhills Supergroup and Gala Group in the northern part of the Southern Uplands, but have also recently been described within the Hawick Group as far south as Kirkcudbright on the Solway coast.

The **Leadhills Supergroup**, of Caradoc to Ashgill age, occurs in the northern part of the Southern Uplands, along the south side of the Southern Uplands Fault, as a series of fault-bounded, largely turbiditic formations. Much of the sequence comprises greywackes, with variable proportions of conglomerates, pebbly sandstones, siltstones, mudstones, cherts and lavas. The sequence reflects variable depositional environments associated with prograding submarine fans, with channel fills, proximal to distal depositional lobes, sheet flows and interchannel deposits. The dominant current directions were towards the southeast and southwest. Sediment provenance varied from acid to ultrabasic igneous basement, to metamorphic rocks with calcareous sedimentary cover, to calc-alkaline island arc rocks. The greywackes vary from feldspathic to quartzose with variable proportions of ferromagnesian minerals. Mineralised veins, including haematite veins, occur in places, such as along faulted valleys.

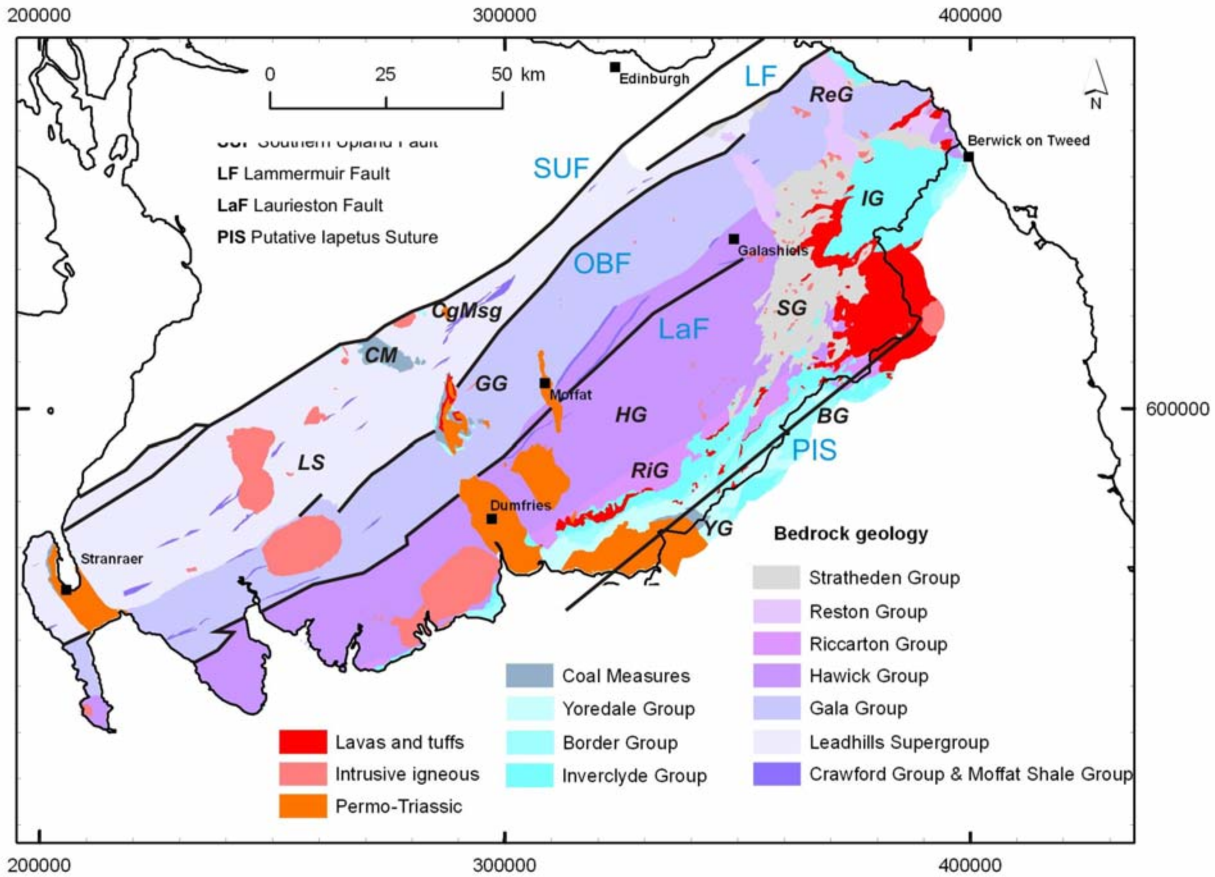


Figure 5 Simplified bedrock geology (from 1:625 000 scale DigMap linework) and structure of southern Scotland, showing major faults

The central part of the Southern Uplands terrane comprises the **Gala Group**, of Llandovery age. This consists of a thick succession of typically medium- to coarse-grained, quartzo-feldspathic greywackes of turbidite origin, which form a series of tectonostratigraphic tracts of very similar sedimentology and composition. These are usually referred to as Gala 1 (the presumed oldest tract at the northern margin of the outcrop) to Gala 8 (the youngest tract at the southern margin of the outcrop. Depositional facies are largely inner to mid-fan sheets, lobes and slumps, with interlobe and channel deposits. Sediment provenance is dominantly acidic plutonic rocks and minor felsic intrusions, with older sedimentary rocks and metamorphic terranes. Current directions are largely towards the southwest or west. There is an overall southward decline in the detrital andesitic component and a trend towards increasing quartz content into the younger, southern strata. Quartz content ranges up to about 55% in some examples from Gala 8; K-feldspar and detrital plagioclase each contribute about 10-15% to the detrital assemblage in the Gala 1 to Gala 6 greywackes, but K-feldspar is less significant in Gala 7 and Gala 8, where plagioclase may make up to 20% of the mineralogy. The decrease in K-feldspar concentration is balanced by an increase in detrital muscovite to form up to 15% in some Gala 8 samples.

The **Hawick Group**, of Llandovery to Wenlock age, is separated from the Gala Group by major strike faults. However, studies have shown that there was physical overlap in the deposition of the two groups, and not simply contemporaneous deposition in two discrete basins. The group consists of thick, uniform sequences of calcareous greywackes, with interbedded siltstones/silty mudstones and minor mudstones. The greywackes are generally fine- to medium-grained amd thinly (centimetre scale) bedded, with occasional medium (metre scale) bedding. Diagenetic calcite makes up most of the calcareous content. By comparison with the Gala Group, the sandstones of the Hawick Group are generally thinner-bedded, finer grained, richer in carbonate and commonly contain detrital haematite-stained mica. The sequence represents turbidite deposits laid down on a mid to outer deep marine fan. Sediment provenance is acidic plutonicic rocks, minor felsic intrusions and older sedimentary rocks, including carbonate sandstone or mudstone.

The **Riccarton Group**, of Wenlock age, occurs in the southern part of the Southern Uplands. The sequence contains a range of facies including channel conglomerates, silty mudstones, thin- to medium-bedded greywackes and thick packets of hemipelagic sediments. The greywackes of this group are richer in quartz, depleted in lithic clasts and have a generally lower carbonate content compared to those of the Hawick Group. The sediments were deposited in upper slope or trench wall environments as well as lobe, channel and overbank, slump and basin plane areas. Sediment was derived from older sedimentary rocks and intermediate minor intrusions, as well as carbonate sand or mud.

The **Reston Group**, of Wenlock (to early Devonian) age outcrops mainly in the valleys of the Lauder Water and the Monynut Water in the northeast of the study area. Smaller outliers occur near Eyemouth and near the Border south of Jedburgh. The Lanark Group is of similar age, but occurs only as very small outcrops along the Southern Upland Fault.

2.2.3 Devonian

Upper Devonian (and related Lower Carboniferous) clastic sedimentary rocks occur as small outcrops along the Southern Uplands Fault between Haddington and Dunbar, further east along the coast at Cockburnspath, between Duns and Slighouses, the largest outlier between Greenlaw and near the border at Carter Bar, and smaller outcrops near Langholm. The rocks belong variously to the Stratheden Group and Inverclyde Group (the latter are sandstones of the Kinnesswood Formation). The rocks are described in detail in Browne et al. (2002); a summary is given here.

Along the coast, the rocks of the **Stratheden Group** include basal conglomerates overlain by shaly sandstones which fine up into red sandy mudstones. Pebbles in the conglomerate are all derived from Lower Palaeozoic greywackes. Some sandstones have calcareous concretions. Imbrication indicates palaeocurrents during sediment deposition were towards the south or southeast. Above this unit is one comprising mainly medium- to coarse-grained red-brown sandstones with thin interbedded red mudstones and siltstones. The sandstones are commonly cross-bedded and include both fluviatile and aeolian facies.

In the smaller Devonian outcrops inland, the Stratheden Group is undivided, comprising largely reddish sandstone and conglomerate, with subordinate mudstone. The conglomerate is dominated by wacke sandstone and Lower Devonian igneous clasts, with a red-brown sandstone matrix. The uppermost units are often calcareous with pedogenic carbonate, often containing cornstone nodules, and are assigned to the Kinnesswood Formation of the Inverclyde Group.

The largest Devonian outlier, in the Greenlaw-Jedburgh-Carter Bar area, is thought to belong largely to the Stratheden Group. The outlier is dominated by reddish, well-rounded sandstones, sometimes pebbly, with minor siltstone, marl and conglomerate beds. The sandstones show a general lack of mica. The lowest units appear to rest unconformably on

Silurian rocks and typically comprise conglomerate. The uppermost outcrops, with pedogenic carbonate, have been assigned to the younger Inverclyde Group.

2.2.4 Carboniferous

Carboniferous rocks occur mainly along the Scotland-England border, with the largest outcrop stretching southwest-northeast from near Dumfries to Carter Bar, and another major outcrop in the Tweed basin (Figure 5). Small outliers occur at Thornhill, at Sanquhar, and on the east coast at Dunbar. The main Carboniferous outcrops of the southern Borders were deposited in a composite ENE-trending half graben encompassing the Solway basin in the west and the Northumberland and Tweed basins in the east, which were partly infilled by debris from the high ground of the Southern Uplands. The successions preserved on the Scottish side of the Border are not as complete as in the Northumberland Basin to the south, where thicknesses of more than 5000 m are preserved.

The older Carboniferous sedimentary facies in the Tweed basin tend to be more proximal than those in the Solway basin, closely resembling Carboniferous facies in the Midland Valley. The lowest units generally overlie Inverclyde Group lavas and are Ballagan-facies deposits of the Inverclyde Group, which include gypsum bands and sporadic fluvial channel sandstones. Occasionally, the lowest units are Kinnesswood Formation (also Inverclyde Group) fluvial deposits with calcretes. The uppermost fluvial sandstones may be equivalent to those of the Clyde Sandstone Formation. They were probably laid down on a semi-arid coastal plain crossed by intermittently flowing, probably meandering, rivers. Increased tectonic activity and runoff from the source area resulted in the appearance of thick fluvial sandstones within the Border Group (Fell Sandstone Formation), which were mostly deposited by braided rivers, although mudstones may comprise 50% to 60% of the group. The succeeding Yoredale Group (Tyne Limestone Formation), partially exposed south of Berwick, contains formerly worked coals and rare marine limestones. The formation resembles the early Namurian Limestone Coal Formation of the Midland Valley, but was subject to stronger marine influences (Read et al. 2002).

The downfaulted Carboniferous outliers at Sanquhar and Thornhill preserve a Namurian mixed sedimentary sequence of the Clackmannan Group, and younger Westphalian Coal Measures, representing depositional environments similar to those in the Midland Valley. The Sanqhar succession includes more than 600 m of Lower, Middle and Upper Coal Measures; at Thornhill the succession is thinner, although contains rocks from the whole Coal Measures succession. Coal Measures probably originally extended over the Solway and Northumberland basins, but were mostly eroded off at the end of the Carboniferous (Read et al. 2002).

2.2.5 Igneous rocks

There are three major intrusive igneous outcrops in the study area, and a number of smaller ones, mostly in Dumfries and Galloway. These are the major granite and granodiorite plutons of Loch Doon, Cairnsmore of Fleet and Criffel-Dalbeatie, and smaller ones such as the Cairnsmore of Carsphairn and Spango plutons. All belong to the Lower Devonian Caledonian Igneous Supersuite.

In the east of the study area there is a major outcrop of volcanic rocks, the Cheviot Lavas of Lower Devonian age, thought to have been generated in a post-collisional setting after the closing of the Iapetus Ocean. Smaller outcrops of andesitic lavas occur around Eyemouth and St Abbs. These have chemical and isotopic affinities to plutons in the northern Southern Uplands, which date from the late Silurian to Lower Devonian (Trewin and Thirlwall 2002).

The Birrenswark Volcanic Formation, around Langholm, is of Lower Carboniferous age and is part of the Inverclyde Group. The Birrenswark Volcanic Formation forms the eastern end of a discontinuous strip of lavas that stretch west almost to Dumfries, which represent an episode of tensional rifting. The formation comprises transitional basalts and hawaiites (Phillips 2000) up to about 90 m thick, with intercalations of reddened sandstone and siltstone. It rests on Lower Palaeozoic rocks or the Lower Carboniferous Kinnesswood Formation, and is overlain conformably by the Ballagan Formation and younger sedimentary strata. In the Tweed Basin, the Kelso Volcanic Formation constitutes a 120 m thick succession of basaltic to hawaiitic lavas and rare volcaniclastic rocks. These are thought to be contemporaneous with the Birrenswark lavas and mark the same tensional episode (Read et al. 2002).

There are at least fifty volcanic conduits and intrusive plugs scattered between Langholm, Jedburgh and Greenlaw, most of which are inferred to mark the conduits through which the lavas of the Birrenswark and Kelso Volcanic Formation erupted, although some northeast of Langholm may have acted as feeders for younger pyroclastic rocks and lavas (Read et al. 2002).

2.2.6 Structure

The Southern Upland Fault forms the boundary between the Southern Uplands and the Midland Valley. It comprises a series of sub-parallel faults along the Caledonian strike (Figure 5) (Floyd 2001, Oliver et al. 2002). The fault is thought to represent both lateral movement of at least 12 km, and variable downthrow to both sides of the fault line.

The Lower Palaeozoic rocks form individual fault-bounded tracts, with the greywackes largely dipping steeply and generally younging towards the northwest. The strike faults trend NE-SW (Figure 5). The original thrusts are thought to be now rotated to near-vertical, and separate northern (including the Leadhills Supergroup), central (including the Gala and Hawick groups) and southern (including the Wenlock Rocks – now known as the Riccarton Group) belts of the Southern Uplands.

The boundary between Ordovician and Silurian rocks (essentially between the Leadhills Supergroup and the Gala Group) is marked by the Orlock Bridge Fault (Oliver et al. 2002) (Figure 5). The fault zone is characterised by numerous shear zones and minor folds.

The south of the study area lies along the general line of the Iapetus suture, arguably the most important fault in Britain, as it forms the boundary between the Avalonian and Laurentian terranes along the Solway Line. However, the suture lies buried beneath the Carboniferous Northumberland basin (Oliver et al. 2002) (Figure 5).

2.3 SUPERFICIAL DEPOSITS

The extent of the superficial deposits in Southern Scotland is shown in Figure 6. Southern Scotland was extensively affected by Quaternary glaciations. The area was ice-covered during the most recent glaciation (the Main Late Devensian), between about 28,000 and 13,000 years before present. This episode accounts for most of the glaciogenic deposits. The highest ground formed sources of ice that flowed outwards over the lower ground. The pattern of ice and glacial meltwater drainage is preserved in the modern drainage pattern. For example, an ice divide in the Tweedsmuir Hills has been identified in the area between Hartfell and Broad Law, from where ice flowed southwest towards the Solway and northeast along the line of the current River Tweed (Everest et al. 2005). This is close to the modern watershed between the Tweed and the Solway catchments. The line of northeasterly ice drainage, along the valley of the Tweed, has been identified as one of the best examples of a palaeo-ice stream known in

Britain, the catchment of which would have included the entire area from the Lammermuirs to the Cheviot Hills (Everest et al. 2005).

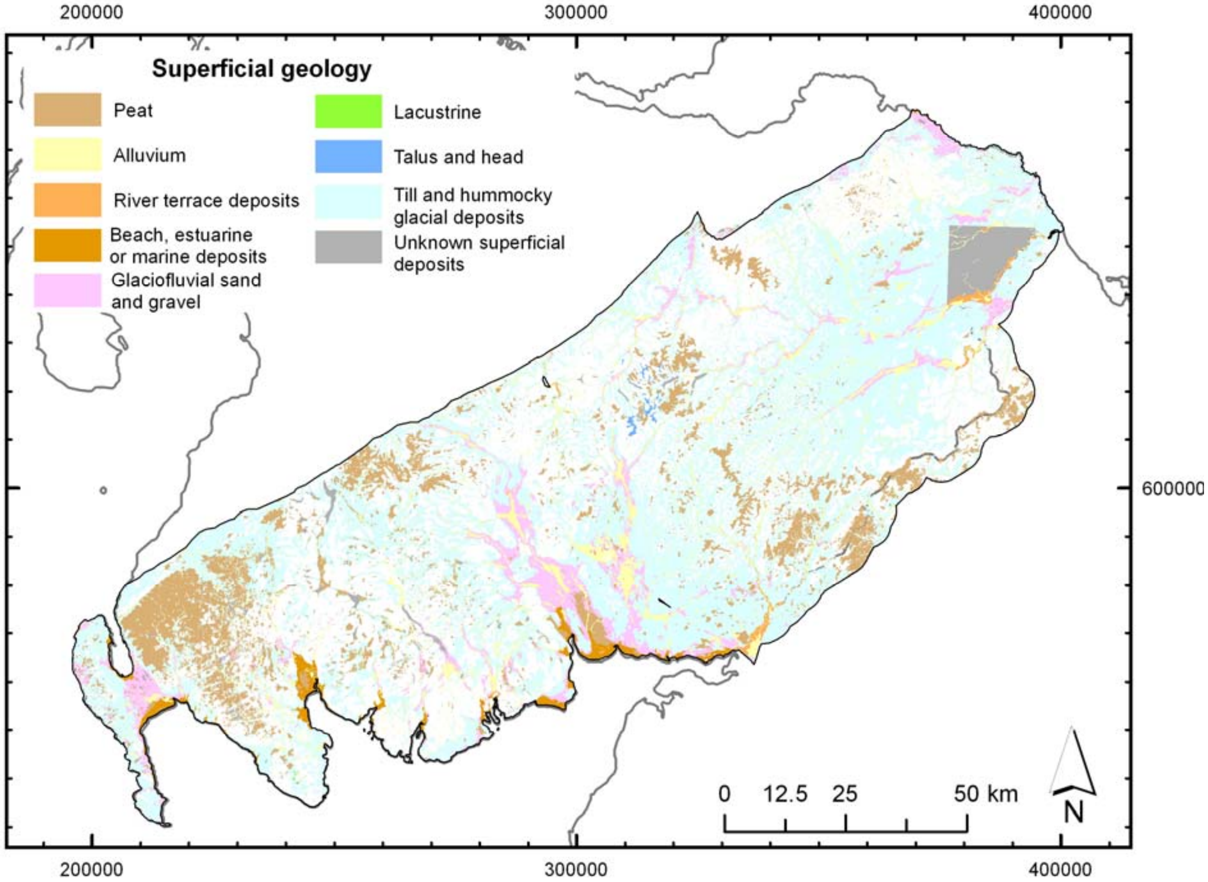


Figure 6 Superficial deposits in southern Scotland.

Across these extensive upland areas, few superficial deposits remain from the last glacial period. Weathered rock occurs, possibly up to 3 m thick, as well as upland deposits such as head. However, no significant Quaternary deposits have been preserved. Blanket peat is present in poorly drained areas.

On the lower ground away from the ice centres, there are extensive glacial deposits. The dominant deposit is a typical glacial lodgement till, which is characteristically silty and clay-rich, often dense and overconsolidated. On hillslopes and higher ground, the till is likely to be less than 3 m thick, but in valleys can be up to 5 m thick, covering the lower slopes and the base of U-shaped, glacially-deepened valleys such as Talla and Fruid. In the Merse area between Coldstream and Duns, up to 60 m of deformed till has been reported (Clapperton 1971), probably representing deposition in successive glacial periods.

Thick glaciofluvial and alluvial deposits have been preserved in the river valleys and in some places along the coast, such as between Dumfries and Gretna, or east of Dunbar. The thickest and most extensive deposits are found in the major valleys such as the Tweed, Annan and Nith, but they are also seen in smaller valleys such as the Teviot, Esk, Yarrow, Dee and Cree. The deposits typically comprise stacked sheets of coarse, poorly sorted, gravelly glacial outwash deposits laid down on the valley floor, into which later terraces have been incised. Recent alluvium has been laid down over the glaciofluvial deposits, at least partly comprising re-worked glaciofluvial material. Evidence from borehole records held by BGS shows that the total thickness of glaciofluvial and alluvial deposits is typically 10 m, and that in some valley areas, such as the Nith valley north of Dumfries, there are at least 20 m of glaciofluvial and alluvial deposits.

Significant estuarine and marine deposits occur along the northern shore of the Solway Firth, particularly around Dumfries and east to Gretna, at Newton Stewart and at Stranraer. These include coarse-grained shoreface and beach shingles and sands and fine-grained tidal-flat and estuarine sands, silts and clays. The deposits can exceed 15 m in thickness, such as at Racks Moss near Dumfries.

There are extensive spreads of peat, largely in upland areas, but also infilling the abandoned estuary southeast of Dumfries where the thickness can exceed 7 m.

2.4 HYDROGEOLOGY

2.4.1 Bedrock hydrogeology

Apart from the Permian Dumfries Basin aquifer (Robins and Ball 2006), there have been no detailed investigations of the physical properties of the aquifers of southern Scotland. The main studies to have touched on this area are Robins (1990), MacDonald et al. (2005), and Ball et al. (in prep).

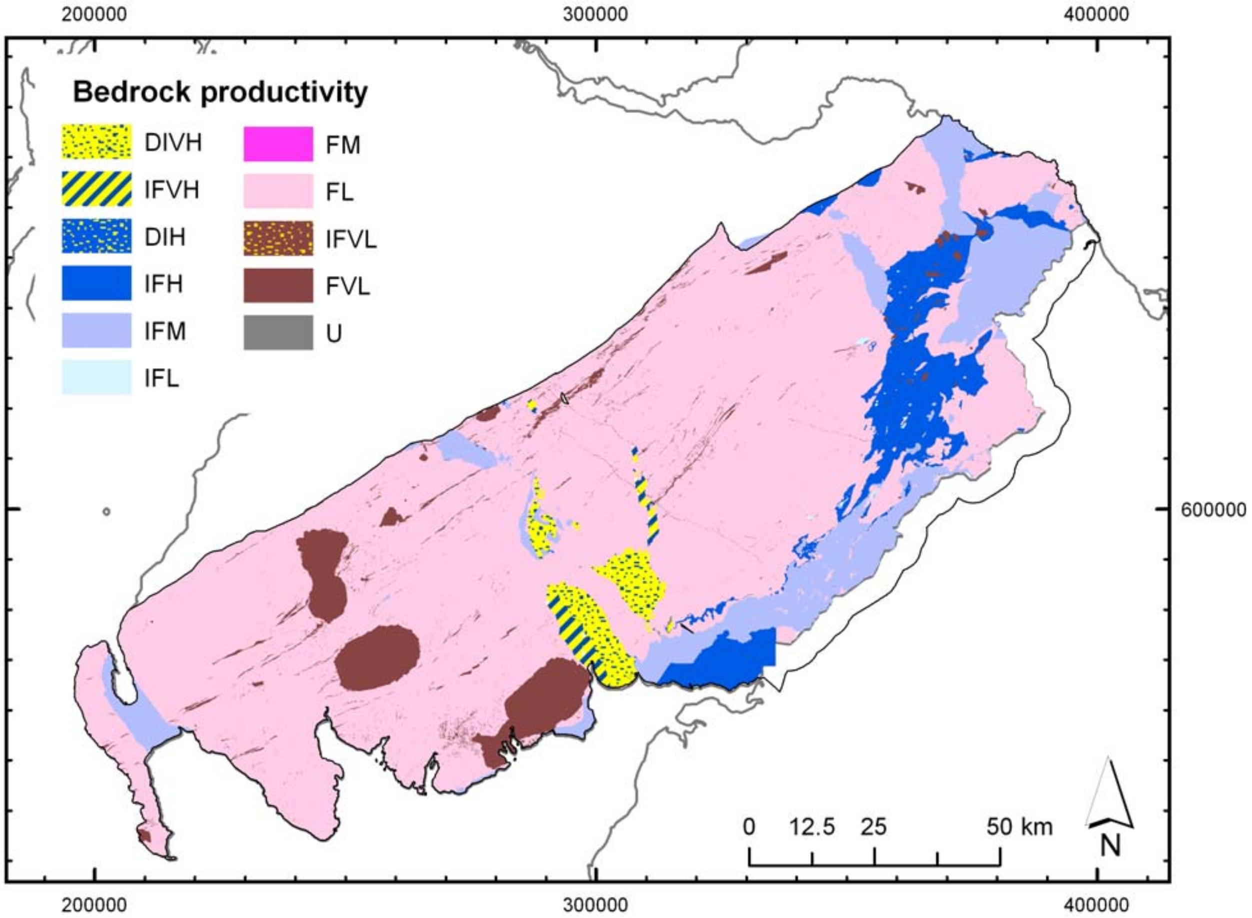
The available information shows that groundwater flow in all the aquifers in southern Scotland is largely through fractures. Intergranular flow is only likely to be significant in the Devonian and Lower Carboniferous sandstones (Figure 7).

The Lower Palaeozoic rocks form low productivity aquifers and individual borehole yields are typically low, ranging from 0.2 to 0.6 $l\ s^{-1}$. No pumping test or core analysis data are available. Typical specific capacity values for the aquifer are in the range 1 to 5 $m^3\ d^{-1}\ m^{-1}$. The dominantly fine-grained, well-cemented nature of the Lower Palaeozoic rocks mean that their intergranular permeability is low. There is often a well-developed weathered zone at rockhead, in which intergranular permeability is enhanced. Below this depth, fractures in the rocks contribute virtually all groundwater storage and flow. Groundwater flow paths in the aquifer are likely to be relatively shallow, short and localised, controlled by fracture patterns.

The Devonian sedimentary rocks generally form the highest productivity aquifers in the study area (with the exception of the Permo-Triassic sandstones; see Figure 7). Recorded borehole yields are typically in the range 1 to 2 $l\ s^{-1}$. In some areas in the Lower Devonian, artesian conditions occur, such as near Earlston. A limited amount of core analysis data is available for the Devonian aquifer in the area (Ball et al. in prep). These data indicate that matrix porosity ranges from 15 to 25% and matrix hydraulic conductivity ranges from 0.0008 to 1.676 $m\ d^{-1}$, with a median value of 0.104 $m\ d^{-1}$. Only four transmissivity values are available for the aquifer, ranging between 1 and 46 $m^2\ d^{-1}$. The Devonian rocks are largely well-cemented with relatively low intergranular permeability. Studies on Devonian sandstones elsewhere in Scotland indicate that intergranular flow can contribute up to 20% of total groundwater flow, but fracture flow is likely to dominate (Ball et al. in prep). Groundwater flow paths are likely to be longer and deeper than in the Palaeozoic rocks. A study in the Devonian aquifer of Strathmore (Ó Dochartaigh et al. 2006) suggested that groundwater was mainly recharged within the past 40 years and mixed throughout the top 100 m of the aquifer.

The Carboniferous sedimentary sequences typically form complex, multi-layered aquifers, in which sandstone units effectively act as discrete aquifers, separated by lower permeability mudstones and coals. Overall, the Carboniferous is thought to form moderately productive aquifers. Recorded borehole yields are typically less than 5 $l\ s^{-1}$. There are no data for physical properties of Carboniferous aquifers in southern Scotland, but based on limited information from the more extensive outcrops of the Midland Valley, the median transmissivity of the Carboniferous aquifers is 150 m^2 d^{-1}, and the median specific capacity is some 50 m^3 d^{-1} m^{-1}. Calculated storage values are typically 0.003 (Ball et al. 2007). Fracture flow dominates groundwater movement in the Carboniferous aquifers, and because of their layered nature, flow paths are likely to be complex.

The igneous rocks in the study area form low productivity aquifers, in which groundwater flow occurs only via fractures. There are few data available on groundwater flow paths or aquifer properties. The few available data from elsewhere in Scotland show that the median specific capacity is around 4 to 5 m^3 d^{-1} m^{-1}; borehole yields are generally less than 1 l s^{-1}; and groundwater flow paths are mainly shallow and short.



DIVH	dominantly intergranular flow, very high productivity	FM	fracture flow, moderate productivity
IFVH	intergranular/fracture flow, very high productivity	FL	fracture flow, low productivity
DIH	dominantly intergranular flow, high productivity	IFVL	intergranular/fracture flow, very low productivity
IFH	intergranular/fracture flow, high productivity	FVL	fracture flow, very low productivity
IFM	intergranular/fracture flow, moderate productivity	U	unknown aquifer productivity
IFL	intergranular/fracture flow, low productivity		

Figure 7 Productivity of bedrock aquifers in southern Scotland (after MacDonald et al. 2005).

2.4.2 Superficial deposits hydrogeology

Where well developed, glaciofluvial and alluvial deposits form highly productive local aquifers in the study area, from which a number of public water supply boreholes abstract.

These include Ringford in the southwest, and Howden, Ettrickbridge, Innerleithen, Yarrowford and Yarrowfeus in the Borders. At least one mineral water borehole also abstracts from a superficial aquifer in the Borders. This report only considers groundwater chemistry in the bedrock aquifers. A future report will consider the chemistry of groundwater in superficial deposits in Scotland.

The highly permeable glaciofluvial and alluvial deposits also allow recharge to infiltrate to the underlying bedrock aquifers. By contrast, where there are thick low permeability clays and silts, recharge to the underlying aquifers is restricted.

2.4.3 Groundwater vulnerability

Across most of the study area, groundwater in the bedrock aquifers is highly vulnerable to pollution from surface activities (Figure 8). This is partly due to the generally thin superficial deposits cover across much of the area, and to the fact that much of the thicker superficial deposits are highly permeable and do not provide significant protection. It also reflects the dominance of fracture permeability in the bedrock aquifers, which can lead to rapid transport of contaminants from the ground surface to the water table. Most of the arable land in the east of the study area lies within a nitrate vulnerable zone, designated on the basis of the high risk land use and known nitrate concentrations in groundwater (Figure 2).

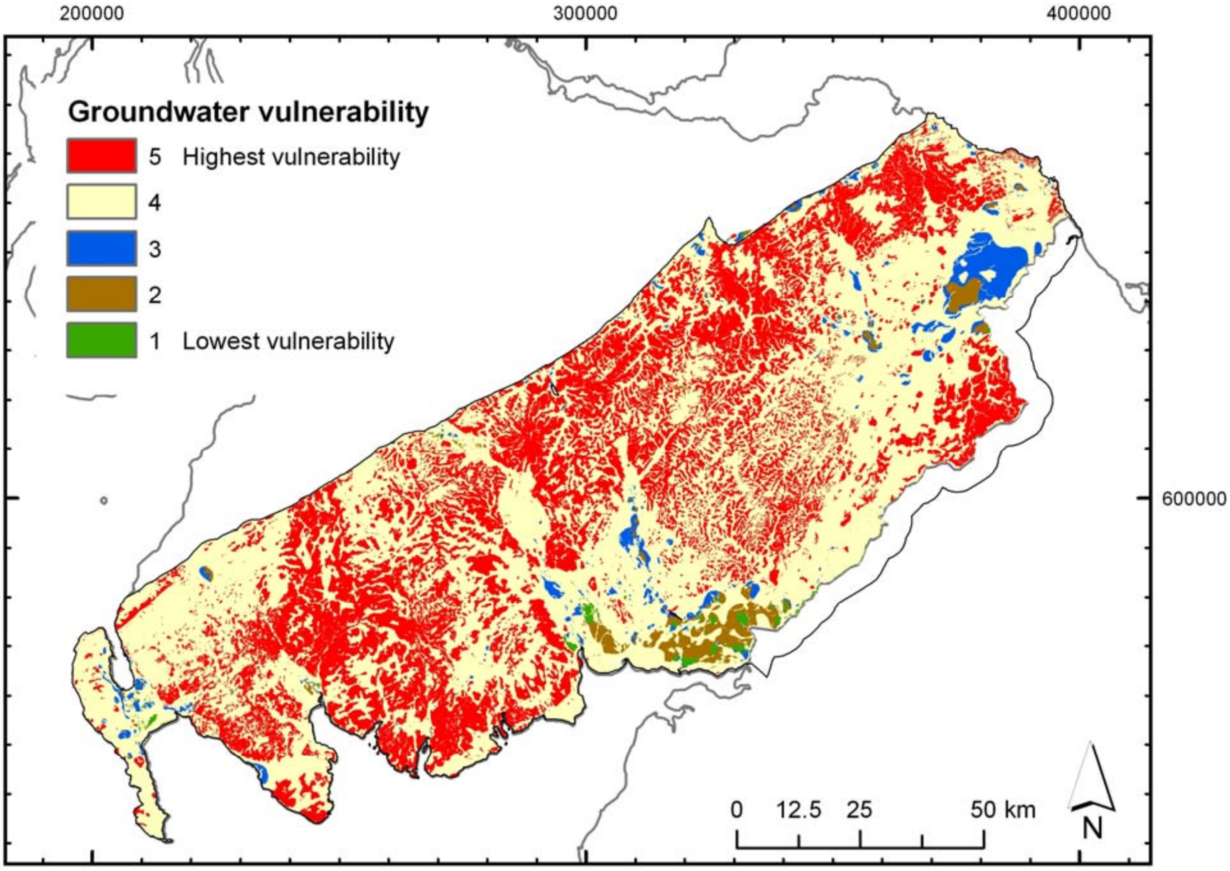


Figure 8 Groundwater vulnerability in southern Scotland

2.4.4 Groundwater use

Historically, springs have been used extensively in southern Scotland for domestic and farm supply and occasionally public supply. Mineralised springs were also an important attraction to the area in the 19th Century with large hydropathic hotels being built in Peebles and Moffat.

Groundwater is still an important resource in southern Scotland and there are at least 1000 individual groundwater sources in the area, with most concentrated in the coastal fringes and major valleys. The vast majority of abstractions are still for private domestic or small farm use. There are also a number of public water supply boreholes, largely drilled into superficial deposits. Other groundwater abstractors are mineral water companies and industries, particularly in textile towns such as Galashiels and Selkirk, and dairies or creameries, particularly in Dumfries and Galloway. In the last few years many new abstraction boreholes have been drilled, mainly for private domestic use, either to replace existing traditional springs or wells or to supply new builds. Figure 9 and Figure 10 show typical housing and headworks of modern domestic boreholes in rural southern Scotland. Below is an estimate of the number of sources on the different aquifers.

- There are at least 900 groundwater abstractions from boreholes, springs and shallow wells in the Lower Palaeozoic aquifer in the Southern Uplands, although full details for many are lacking. The majority of abstractions are for private domestic or small farm use. There are no recorded abstractions from large parts of the Lower Palaeozoic outcrop, particularly the upland areas where population is sparse.
- There are approximately 100 small abstractions from the Devonian aquifer in southern Scotland, largely for domestic and farm use. There are likely to be many more unrecorded springs and shallow wells. There are no records of large abstractions or public water supply.
- There are at least 50 abstractions from the Carboniferous aquifer in southern Scotland, mostly farm boreholes in the Tweed basin.
- There are a small number of abstractions from igneous rocks in the study area, again largely farm springs and boreholes.

Figure 9 Typical shed housing for borehole used for rural farm supply

Figure 10 Typical well head construction of private boreholes in southern Scotland. The floor is cemented and the borehole open, but protected within a small shed.

Groundwater formed an important part in the development of the hydropathic movement in Scotland during the 19th century (Bradley et al. 1997, Spence and Robins 2004). Two sources of mineralised water were particularly important in sustaining a thriving spa industry: St Ronan's Well in Innerleithen and Garpol Spa, Hartfell Spa and Moffat Well in and around Moffat. The discussions below are based on information available from the local tourist board.

The earliest known written account of St Ronan's Well was discovered in a Statistical Account of Scotland in 1795-97, although Robert Burns may have sampled the waters in 1780. Local folklore suggests that two girls were cured of near blindness from taking the waters for a period of time. Doctor Fyfe, a local physician in the 1820s, suggested that the water was also useful for curing bile, stomach complaints, scurvy, sterility and "general debility of the system". A chemist, Stevenson Macadam, analysed the waters in 1896 and found two different mineralised springs: a saline spring and a sulphurous spring. Only a freshwater spring and the sulphurous spring were found during fieldwork in 2005.

The mineralised springs around Moffat appear to have been developed earlier than St Ronan's Well (Figure 11). In 1748 a local farmer, John Williamson, discovered the chalybeate water of Hartfell Spa while prospecting and mining for copper. This was reputed to be of great benefit to sufferers of chest ailments. It was believed that, unlike other mineral waters, the water could be bottled and stored without any effect on the healing qualities, and it was even shipped to India and the West Indies by the 19th century physician Dr Johnston.

The sulphurous Moffat Well was found in 1633 by Rachel Whyteford. The water was believed to help cure most illnesses and bathing in it was claimed to cure most skin complaints, although the treatment had to be continued over several weeks to see improvement. In 1758, Dr Hunter, a physician in Moffat, began to improve access to the well and a small stone house was built along with a new bridge and road. The recognised time to take the water was 7 am and waiting visitors were kept amused by a piper. Along with other hydropathic establishments, belief in the curative properties of the waters declined in the early to mid 20th century.

Figure 11 The mineralised springs of Hartfell Spa (left) and Moffat Well (right), near Moffat.

At least two of these springs (Hartfell Spa and Moffat Well) are thought to be associated with the Moffat Shale Group. Four of the springs (Hartfell Spa, Moffat Well, St Ronan's Sulphur Spring and St Ronan's Fresh Spring) were sampled as part of the current project.

2.5 AQUIFER GEOCHEMISTRY FROM G-BASE

2.5.1 Stream sediment information

An assessment of the mineralogy of the aquifers in the study area has been made based on stream sediment geochemistry data collected and analysed as part of the BGS national Geochemical Baseline Survey of the Environment (G-BASE), which has been reported for southern Scotland by BGS (1993). In most cases stream sediment geochemistry primarily reflects geology and geological mineralisation, although in some cases, anthropogenic factors such as agriculture and urbanisation have modified the response of stream sediments to the bedrock.

The following patterns in selected element distribution in bedrock across the study area have been inferred from the stream sediment geochemistry.

Calcium, controlled by the calcareous content of the bedrock, is at highest concentrations in sediments overlying the Carboniferous limestones of east Berwickshire, and is also high over other Carboniferous rocks in the area (Figure 5). Locally enhanced values over Carboniferous rocks around Kelso correspond to the presence of calcite nodules (cornstones). High Ca concentrations are also seen over the Loch Doon pluton. There are moderate concentrations over the Hawick Group, and the lowest concentrations are seen over the north Gala Group and the Riccarton and Reston Groups.

Magnesium is moderately high to high over the calcareous Hawick Group, the south Gala Group, the most pyroxene-rich units of the Leadhills Group, and basic-intermediate igneous intrusions such as the Cairnsmore of Carsphairn pluton. It is lowest over most Carboniferous lithologies, reflecting the non-dolomitic nature of the carbonate facies. There are also low concentrations over the Cairnsmore of Fleet pluton and over lavas at Kelso, despite their known Mg enrichment, possibly due to anthropogenic modifications.

Across the Southern Uplands, the most striking regional geochemical feature is a fine striping in element concentrations along a NE-SW trend, running parallel to the regional strike of the Ordovician and Silurian beds, which reflects variations in rock composition. This is seen particularly across the Gala and Hawick groups by high concentrations of the metals chromium (Cr), which is particularly elevated, nickel (Ni), vanadium (V) and associated zirconium (Zr), which are inferred to be derived from ophiolitic rocks (Stone et al. 2003).

The northern, back-arc, sediments of the Southern Uplands are enriched in arsenic relative to the more feldspathic foreland basin deposits of the southern Gala Group and Hawick, Riccarton and Reston Groups. The median arsenic concentration over Ordovician units and the north Gala Group greywackes is in the range 18 to 22 mg kg^{-1}, compared with values of 10 to 13 mg kg^{-1} over the south Gala, Hawick and Riccarton groups. Significant, although areally small, arsenic haloes of more than 85 mg kg^{-1} occur around the Loch Doon and Cairnsmore of Fleet granitic plutons, and the surrounding Gala Group.

The Ordovician strata of the northern Southern Uplands are depleted in lead (< 50 mg kg^{-1}) relative to the Silurian greywacke sequences to the south (50 – 90 mg kg^{-1}), reflecting changes in provenance of the sediments. Lead concentrations are enhanced in the Moffat Shale Group relative to other rock types in the area. The Leadhills-Wanlockhead area has been exploited for lead since Roman times, and the ‘natural’ stream sediment signatures for the area are largely masked by the influence of minespoil. Lead concentrations up to 10 000 mg kg^{-1} are reported in the area (BGS 1993).

Uranium concentrations are highest over the granitic intrusions, and are also high over the Cheviot volcanic complex. Elsewhere, moderately high values occur over the Gala Group, with the lowest values over the Ordovician. Uranium was also measured in stream waters, which showed some higher values associated with high pH and/or high concentrations of dissolved bicarbonate, such as in the area of the calcareous Carboniferous sedimentary rocks in east Berwickshire. Higher values also occur over the Cairnsmore of Fleet and Criffel-Dalbeattie plutons.

2.5.2 Stream water information

The limited stream water chemistry data available from the G-BASE database show that distinct variations exist across the aquifers in the study area. Stream water pH is typically alkaline over the calcareous greywackes of the Hawick, Riccarton and Reston Groups, and the Carboniferous rocks of the Tweed and Solway basins (Figure 12). Acidic stream waters occur particularly over the Loch Doon and Cairnsmore of Fleet granite plutons, but less so over the Criffel-Dalbeattie pluton. Acidic stream waters also occur over Ordovician and Gala Group rocks to the west of the Loch Doon and Cairnsmore of Fleet plutons.

Stream water conductivity (SEC) is highest (> 500 µS cm^{-1}) over Carboniferous Limestone strata in east Berwickshire, and moderately high (generally 200 – 500 µS cm^{-1}) over the rest of the Carboniferous outcrops. Moderately high values (200 to 350 µS cm^{-1}) are observed over the Hawick Group, coinciding with increasing concentrations of Ca, Mg and total carbonate in the greywackes, although the increased use of agricultural fertilisers over the lower, more fertile sectors of the south Gala and Hawick groups are also likely to be an influence. By contrast, low SEC values (< 200 µS cm^{-1}) occur over the Leadhills Group and northern Gala Group, reflecting predominantly quartzose and pyroxene-rich facies.

Stream water shows low to moderate concentrations of bicarbonate (3 to 40 mg l^{-1}) over the Leadhills and Gala groups and the Riccarton and Reston Groups, interrupted by a zone of higher values (c. 80 mg l^{-1}) over the Hawick Group, reflecting an abrupt increase in bedrock $CaCO_3$ content. The highest stream water bicarbonate concentrations (100 to over 200 mg l^{-1})

occur over the Carboniferous limestones in east Berwickshire, with relatively high concentrations (50 to 160 mg l^{-1}) over the Carboniferous rocks of the Solway basin.

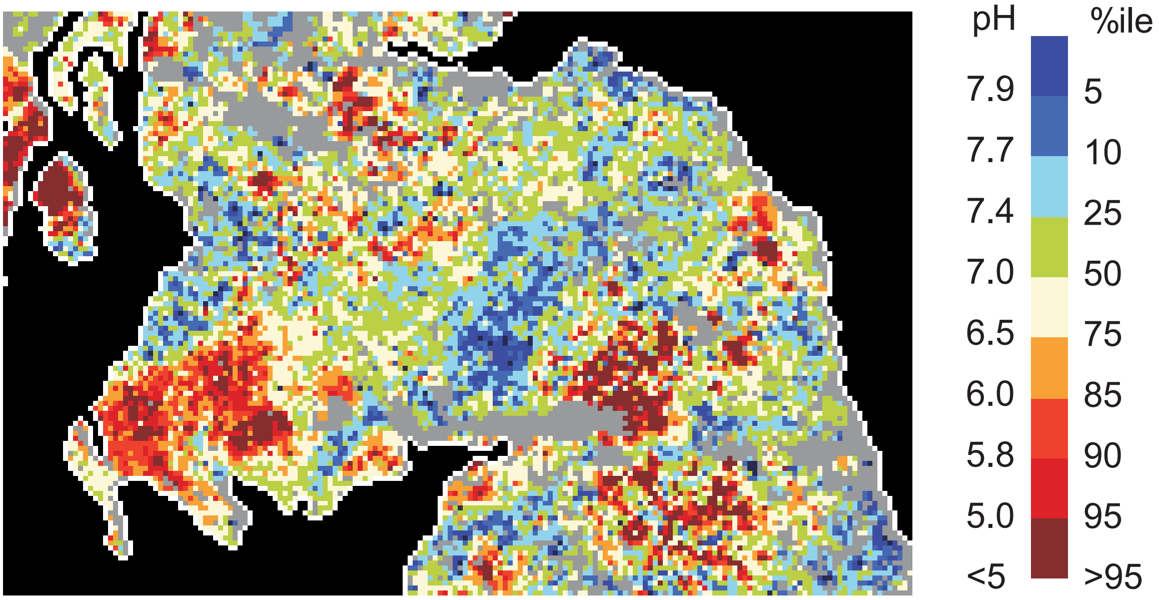


Figure 12 pH in stream water for southern Scotland and northern England (from BGS 1993).

Fluoride concentrations in stream waters are highest over Devonian and Carboniferous sedimentary rocks, particularly over limestone and coaliferous facies in east Berwickshire. There are also relatively high concentrations over the Cairnsmore of Fleet granite pluton. There is some internal variation over Silurian and Ordovician rocks, such that over the more calcareous facies of the Hawick Group, stream waters show systematically higher fluoride concentrations (c. 0.05 mg l^{-1}) than over more quartzo-feldspathic units such as the Gala Group (< 0.04 mg l^{-1}).

2.6 RAINFALL CHEMISTRY

Rainfall chemistry data are available from three stations across the study area – at Loch Dee in the west, Eskdalemuir in the central part and Whiteadder in the northeast (Table 1). The stations lie at similar altitudes, but clearly show the west-east split in rainfall patterns in Scotland, with the average annual rainfall at Loch Dee in the west, over 1600 mm, nearly three times the equivalent at Whiteadder in the east, at less than 600 mm. The rainfall volumes and chemistry are taken as the average for the period 2000 to 2005.

Solutes derived from rainfall typically increase during evapotranspiration, such that the solute concentration in infiltrating recharge under ambient climatic conditions is expected to be roughly three times higher than in rainfall. However, nutrient concentrations (e.g. nitrogen and potassium) may decrease due to biomass uptake, so that infiltrating (recharge) waters may contain lower concentrations of these solutes than the evaporated rainfall. Ammonium would be expected to at least partially oxidise to nitrate on infiltration. An estimate of the likely chemistry of infiltrating recharge water after evapotranspiration, based on rainfall chemistry for 2000-2005 from the three monitoring stations, is also presented (Table 1).

Table 1 Rainfall chemistry at monitoring stations in southern Scotland, from the UK National Air Quality Information Archive (http://www.airquality.co.uk/archive/index.php)

	Units	Loch Dee	Eskdalemuir	Whiteadder	Expected chemistry of infiltrating recharge after evapotranspiration[1]
NGR		NX 468 779	NT 235 030	NT 664 633	
Elevation	m OD	230	259	250	
Annual rainfall	mm	1633	1358	586	
		Median 2000-2005	Median 2000-2005	Median 2000-2005	
pH	-	5.23	5.05	4.70	-
SEC	µS cm^{-1}	26.00	20.00	25.00	71
Ca	mg l^{-1}	0.14	0.10	0.17	0.42
Cl	mg l^{-1}	2.81	2.01	2.11	6.9
K	mg l^{-1}	0.14	0.08	0.11	0.33
Mg	mg l^{-1}	0.17	0.13	0.16	0.47
NH_4-N	mg l^{-1}	0.40	0.30	0.33	-
NO_3-N	mg l^{-1}	0.18	0.25	0.31	0.73
Na	mg l^{-1}	1.64	1.13	1.26	4.0
PO_4-P	mg l^{-1}	<0.01	<0.01	<0.01	<0.03
SO_4-S	mg l^{-1}	0.55	0.41	0.58	1.5

[1] Calculated for illustrative purposes as three times the median rainfall concentration averaged across the monitoring stations

3 Methodology

3.1 INTRODUCTION

A total of 47 new groundwater samples were collected for analysis from the Lower Palaeozoic, Devonian, Carboniferous and igneous aquifers in the study area during this project. Of these, 25 were collected from the Borders between September and November 2005, and 22 were collected from Dumfries and Galloway in July 2006. These new samples were augmented with a further 31 samples collected during separate projects: 14 in April and May 2005 as part of a project to review the effectiveness of Scotland's national groundwater nitrate monitoring network (MacDonald et al. 2005); 11 during December 2001 as part of a project to identify suitable points for groundwater sampling in areas proposed as nitrate vulnerable zones (NVZ) (Ball and MacDonald 2002); five during September 2004 as part of a survey of nitrate concentrations in groundwater in the Nithsdale NVZ (MacDonald and Abesser 2004); and one in July 2006 as part of a small groundwater investigation project (Ó Dochartaigh 2006). These earlier samples fill in many of the gaps in sample collection across the study area. Many of the additional samples were collected from sites targeted to agricultural areas, which now form part of the current SEPA groundwater quality network (MacDonald et al. 2005). A quality assurance process was followed to ensure only samples from high quality groundwater sources, which are unlikely to be directly impacted by any agricultural contamination, were included.

3.2 SITES SAMPLED

The criteria for site selection during the Baseline sampling survey were:

- to collect a suitable number of samples from each of the studied aquifer types, according to the distribution and areal extent of the aquifers;
- to collect samples distributed as evenly as possible over each of the aquifer types studied; and
- to collect samples that were as far as possible representative of groundwater in the studied aquifers.

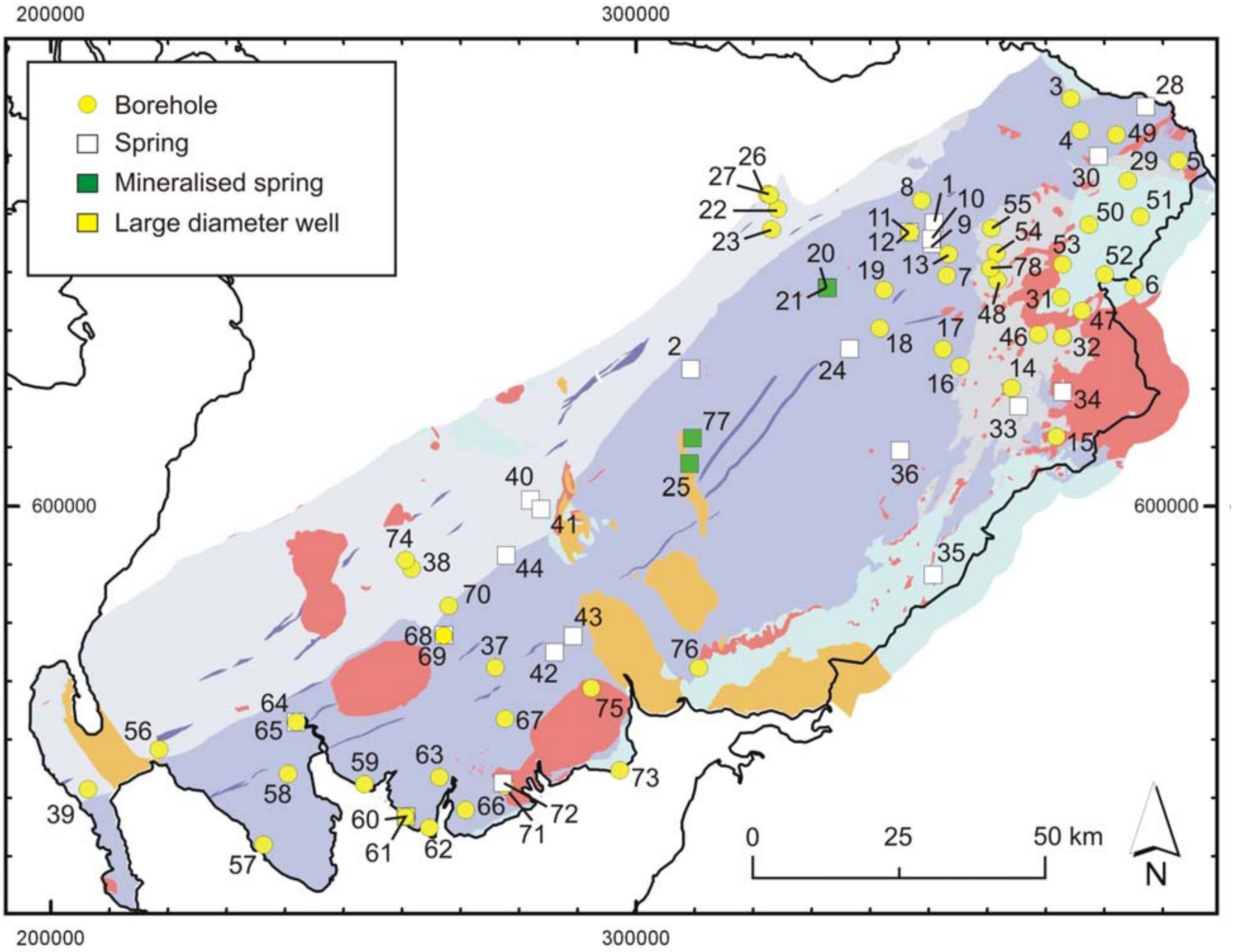
The criteria for site selection during the earlier studies from which samples were included varied, but in general matched the second and third of the criteria above. The criteria for selecting additional samples from these studies to be used in the current Baseline project included the suitable location and distribution of samples across the studied Baseline aquifers, according to the distribution and areal extent of the aquifers, and suitable sampling and analysis procedure.

The sites for all samples used in the study were chosen to be representative of groundwater in the local area. Sources that were very poorly constructed – e.g. open and/or uncased boreholes in leaking chambers – and which were close to obvious and significant sources of contamination – e.g. unsecured slurry stores – were avoided.

Each of the sample sites was assessed at the time of sampling, in particular the source construction and the surrounding land use, to identify any potential sources of contamination that could affect the chemistry of sampled groundwater and the risk of contamination.

The location of the sampling points is shown in Figure 13. Details of the distribution of samples across source type, aquifer and land use are given in Table 2.

Most of the samples were collected from boreholes. In most cases, the sampled boreholes had been pumped regularly in the few weeks leading up to sampling, and were pumping at the time of sampling. Hence, groundwater samples were believed to be as representative of *in-situ* groundwater as possible. Where boreholes were not pumping on arrival, they were pumped for at least 10 minutes to allow purging before sample collection. Pumped groundwater samples represent the compositions of water entering the borehole over its open-hole section. As such, the sample may represent a mixture of waters with different chemistry, especially where the borehole screen extends over more than one fracture inflow.



For key to geology see Figure 5.

Figure 13 Location of groundwater samples, showing groundwater source type and bedrock geology.

A smaller proportion of the samples were collected from springs. Because springs are constantly flowing, they are naturally purged, and the sampled groundwater is therefore likely to be representative of groundwater in the surrounding aquifer.

One of the samples was collected from a shallow well, which are often poor sampling points because they are difficult to purge. In this case, the well was in daily use and the sample obtained is likely to be representative. Springs and wells typically tap shallow groundwater and have relatively small catchments, and so are less likely than boreholes to represent a mixture of groundwaters from different depths.

Table 2 Summary of samples by geology, surrounding land use and source type

Land use	**Arable**			**Mixed agricultural**			**Pasture**			**Pasture DPP**[1]			**Recreational**			**Semi natural**			**Woodland**			**Total**
Geology	B[2]	S[2]	W[2]	B	S	W	B	S	W	B	S	W	B	S	W	B	S	W	B	S	W	
Carboniferous	2			4			1						2							1		10
Devonian	3			3	1		3						1						2			13
Igneous							1	1								1	1					4
Ordovician										4						3	1					8
Silurian	2	1					10	8	1	2	1		2			7	5			1		40
Lower Palaeozoic mineralized																1	2					3
Total	7	1	0	7	1	0	15	9	1	6	1	0	5	0	0	12	9	0	2	2	0	**78**
	8			8			25			7			5			21			4			

[1] DPP – Dairy, Pigs and Poultry

[2] B – Borehole; S – Spring; W – Well

3.3 SAMPLING PROCEDURE

At each sample site, field measurements were made of pH, dissolved oxygen (DO), redox potential (Eh), water temperature, specific electrical conductance (SEC) and alkalinity. Where possible, pH, DO and Eh were measured in an in-line flow cell to minimise atmospheric contamination and parameters were monitored (typically for 10 to 15 minutes) until stable readings were obtained. Where not possible, measurements of water direct from the pump outlet were made in a bucket within one to two minutes of abstraction.

Water samples were also collected for subsequent laboratory analysis. Samples for major- and trace-element analysis were filtered through 0.45 µm filters and collected in polyethylene bottles rinsed with sample water before collection. Four filtered aliquots were collected at each site: two were acidified to 1% v/v with Aristar HNO_3, one for analysis of major cations, total sulphur and Si by ICP-OES (inductively coupled plasma-optical emission spectroscopy), and the other for a large range of trace elements by ICP-MS (inductively coupled plasma mass spectrometry). A third aliquot was acidified to 1% v/v with Aristar HCl for analysis of As by AFS (atomic fluorescence spectrometry) with hydride generation, to be used if necessary as a check on ICP-MS As analyses. A fourth aliquot was left unacidified for analysis of anions by ion chromatography (Cl, NO_3-N, Br, F) and automated colorimetry (NO_2-N, NH_4-N). Samples were also collected in chromic-acid-washed glass bottles for dissolved organic carbon (DOC) analysis, after filtration using silver-impregnated 0.45 µm filters. DOC was measured by carbon analyser. At 15 of the sample sites, additional water samples were collected in glass bottles for stable-isotopic analyses (δ^2H, $\delta^{18}O$ and $\delta^{13}C$). At 9 of the sites, a sample was also collected for CFC analysis in a glass bottle, submerged under flowing groundwater to prevent atmospheric contamination. Most analyses were carried out at the BGS laboratories in Wallingford, except for ICP-MS analysis which was carried out by ACME laboratories, Vancouver, Canada.

Analyses of total sulphur are hereafter expressed as SO_4 and alkalinity as HCO_3. Analyses of $\delta^{2}H$, $\delta^{18}O$ are expressed as per mil deviations relative to VSMOW (Vienna Standard Mean Ocean Water) and $\delta^{13}C$ relative to VPDB (Vienna Pee Dee Belemnite).

The average absolute charge imbalance was 1.6% and the maximum imbalance was 6.3%. This gives confidence that the analytical results for the major species of all samples are reliable. The BGS Wallingford laboratories run a series of QA checks, including analysis of certified standards, to ensure that all analyses are within their prescribed limits.

4 Hydrogeochemistry

4.1 DATA ANALYSIS AND PRESENTATION

4.1.1 Summary statistics

Groundwater quality data are available for a total of 78 sites spread across the study area. Where these are identified and discussed individually in this report, they are referred to by a numerical ID. Summary details of each of these sample sites are given in Appendix 1. Summary statistics were calculated for each of the measured parameters (see Discussion). These provide an indication of the range of values observed and can be compared with similar tables from other areas. The median value provides the preferred estimate of the 'central tendency' for a particular dataset since it is unaffected by outliers. We have also included maximum and minimum values to show the extreme values observed in the dataset.

The summary statistics were reported in terms of percentiles to provide a non-parametric summary of the distribution. Data for many of the trace elements were close to or below their respective instrumental detection limits (or reporting limits), which can complicate the calculation of the summary statistics. The total number of observations and the number of censored (below detection limit) observations are also reported to indicate the degree of censoring.

While the calculation of the median value is less sensitive to censoring than a calculation of the mean value, some of the datasets contained multiple detection limits or had more than 50% censored values. Many authors use a method of substitution to circumvent the problem of censoring, most frequently using half the detection limit for all censored values, but Helsel (2005) strongly criticises this approach. He recommends using a more statistically sound approach and describes three such approaches: (i) the Kaplan-Meier (KM) non-parametric method; (ii) a robust 'regression on order' statistics ('ROS') approach, and (iii) a maximum likelihood ('MLE') method.

We used the non-parametric Kaplan-Meier approach for most datasets but where the censoring was above 50%, we used the ROS approach, following the recommendation of Lee and Helsel (2007). We have not used the MLE approach, or half detection limits in reporting any of the data. . The calculations were made using the NADA package Version 1.5 run in the 'R' working environment (Lee and Helsel, 2005; R Development Core Team, 2007).

Where possible, calculations were made using the raw analytical data rather than the censored data. However, in constructing the table of summary statistics, we applied censoring to any estimates below the typical censored value to ensure that the reported statistics represented the variation of the aquifers involved rather than the errors of the analytical method used.

4.1.2 Example: applying KM, ROS, MLE and ½ detection limit to arsenic data

An example of the application of the various methods for dealing with censored data is given below using the As data. These data were determined by ICP-MS. 44 out of 78 (56%) samples were below the detection limit of 0.5 µg/l: i.e. it is heavily censored.

A number of methods have been employed for dealing with censored data. These have been most widely employed in 'survival statistics' where the period of observation is, for example, not long enough to observe someone's death. This produces so-called right-censored data (e.g., patient 'X' survived more than 'Y' years).

The situation in environmental chemistry is somewhat similar except that a sample is said to have a concentration lower than a certain value. This is left-censoring. It is possible to convert left-censored data to right-censored data by subtracting a number larger than the greatest concentration from each value. This then enables the methods developed for survival statistics to be used simply by 'flipping' the original data.

Dealing with censored data in this way has not been readily taken up in the environmental sciences, although it has been discussed in the environmental literature for more than 40 years (Helsel 2005). It should become more commonly used as the required software becomes more widely available.

We demonstrate some examples of the various possible approaches here. These vary in the type of data that they can deal with and in the assumptions about the underlying distribution that are made.

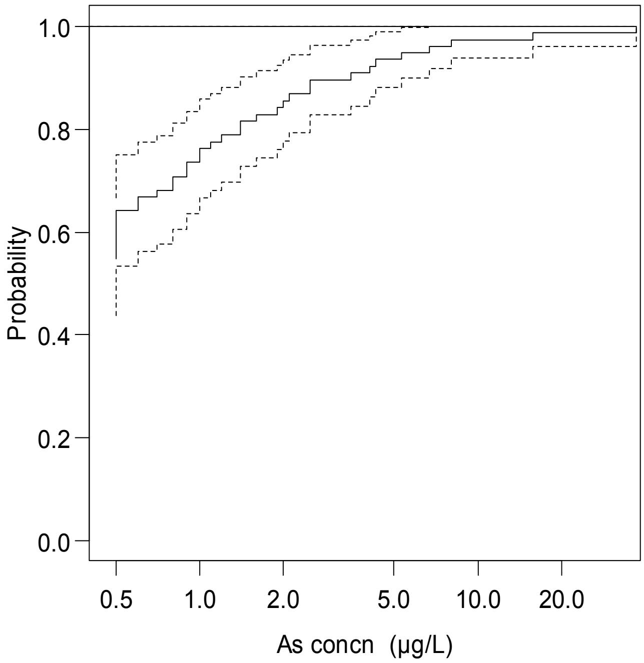
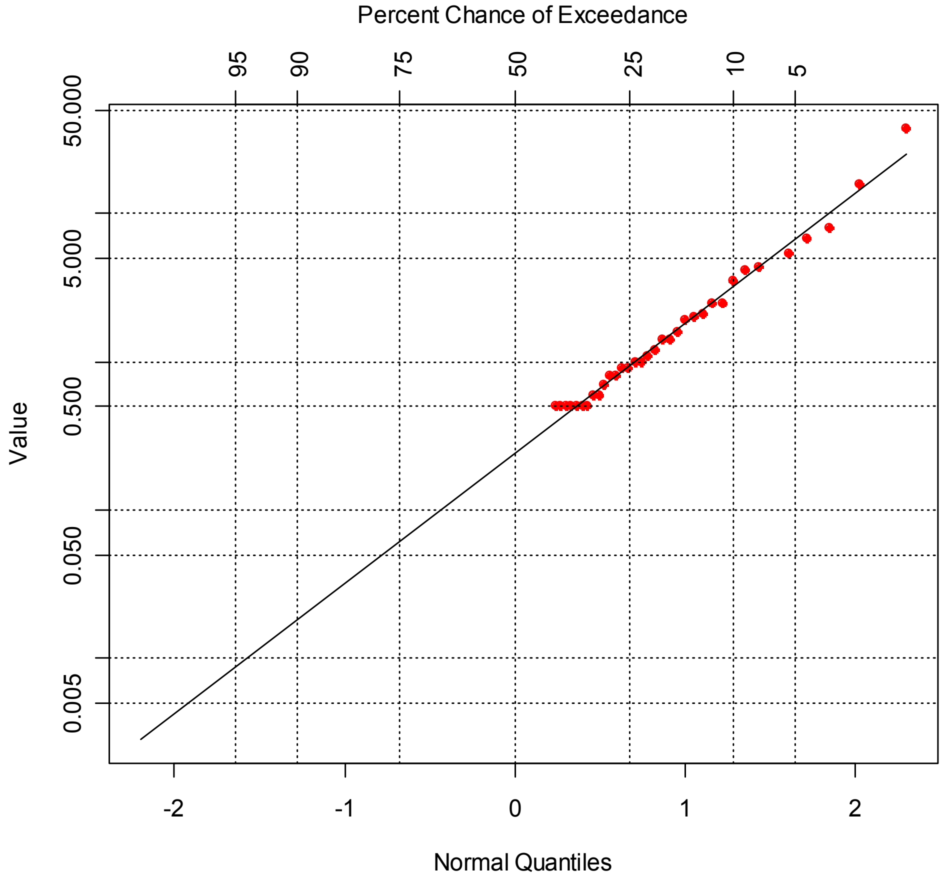


Figure 14 Probability (cumulative frequency) plot for the As data calculated according to the Kaplan-Meier method for dealing with censored data. A log concentration scale is used for displaying the data

The Kaplan-Meier method is a non-parametric procedure that produces a step function and is based on the fact that the probability that a concentration exceeds a particular value can be calculated from the product of the conditional probabilities for finding values found at higher concentrations. The probability (cumulative frequency) plot for As for southern Scotland derived with this approach is shown in Figure 14. It does not extend below the lowest censoring value (0.5 µg/l), but allows statistics above the censored data to be reported.

'ROS' ('Regression on Order Statistics') methods use a regression equation derived from a probability plot to estimate summary statistics. Several options exist but the method applied here is the 'robust' method of Helsel (2005) which uses the sample data to estimate percentiles for values above the maximum censored value and only uses the regression equation for lower concentrations. It is therefore partially parametric.

The robust ROS method computes the Weibull-type plotting positions of the combined uncensored and censored observations using a formula designed for multiply-censored data. A linear regression is then calculated for the log-transformed data using the plotting positions of the uncensored observations and their normal quantiles (Figure 15, red symbols). In our As example, the uncensored data follow the log normal distribution closely, justifying a log-transformation of the data prior to analysis.



Red symbols are uncensored values. The black line is the best-fitting regression line, which is extended into the censored region

Figure 15 Fit of the regression ('ROS') model to the As data.

Once the fitted regression model has been derived (Figure 15, black line), it can be used to estimate the concentration of the censored observations as a function of their normal quantiles. Then the observed uncensored values can be combined with these modelled values to estimate summary statistics for the entire population. By combining the uncensored values with modelled censored values, this method is more resistant to any non-normality of errors, and reduces any transformation errors that may be incurred. The estimated median concentration in this example was 0.27 µg/l.

The maximum likelihood or MLE approach is somewhat similar to the ROS approach. It relies on the data following a known distribution (normal or log-normal). In practice, this approach does not appear to work well for small (*n* < 30) datasets, particularly those assuming a lognormal distribution (Helsel 2005).

Table 3 Summary statistics for the southern Scotland As data using three different approaches for dealing with the censored data

Method	Mean	P25%	P50%	P75%	P90%	P95%
			As (µg/l)			
ROS	1.52	0.07	0.27	0.98	2.80	5.51
KM	1.74	NA	NA	1.00	3.50	6.70
MLE	1.44	0.13	0.38	1.15	3.09	5.58
1/2DL	1.68	0.25	0.25	1.20	2.80	5.51

NA: not available. See below

A summary of the statistics obtained by applying these methods is given in Table 3. The 'half detection limit' substitution approach ('1/2DL' method) is also included. In this case, the 1/2DL method gives the same results as the ROS method at high concentrations but considerably overestimates the concentrations at low percentiles where censoring is operating. Note that the KM method cannot give an estimate for percentiles affected by censoring and so reports 'NA' (not available). In summary tables, these values are best substituted by less than the censored value, which here is <0.5 µg/l.

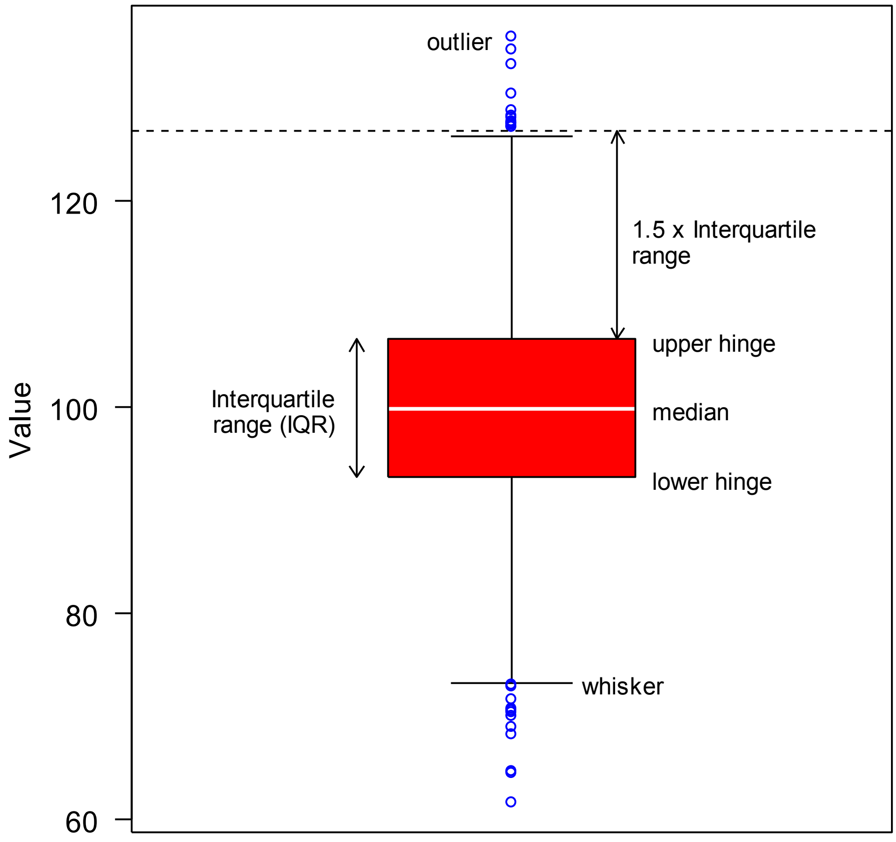
4.1.3 Maps

'Bubble' maps were used to display the spatial distribution of the various water quality parameters. These were generated in 'R' using the `PBSmapping` and `maptools` packages using shapefiles generated by the BGS ArcGIS mapping software. Standard BGS colours were used for the geological base map incorporated with the groundwater quality maps. In general, four classes were used for simplicity, with the size and colour of the plotting symbol varying with class. Class limits were broadly based on the 25, 50 and 90 percentiles. These were simplified where there were insufficient distinct values to generate reliable percentiles.

4.1.4 Boxplots

Boxplots provide a quick graphical summary of the distribution of data values in a dataset and give an excellent way of comparing different values. They provide a rapid view of the central tendency (the median), the spread of values (the interquartile range or box size) and the presence of outliers (beyond the whiskers) (Figure 16). Note that the presence of outliers depends to some extent on the number of values summarised, as even perfectly 'normal' distributions can show outliers if there are sufficient values within the distribution, as in Figure 16.

Helsel (2005) discusses how the classical boxplot can be adapted for displaying distributions containing censored data.



The whiskers are placed at the most extreme values, that in this case fall within a distance of no more than 1.5 × IQR from the nearest hinge. Outliers lie beyond this.

Figure 16 Annotated boxplot based on a simulated normal distribution of 2000 values with mean = 100 and standard deviation = 10.

4.1.5 Classifying the data

We have divided the data on the basis of bedrock geology of the aquifer from which the sample was taken. There can be other important, and perhaps dominant, factors for specific chemical parameters, but rock type is perhaps the single most useful one in the present context.

The samples were classified into four main chronostratigraphic bedrock groups: Ordovician, Silurian, Devonian and Carboniferous. There are also a small number (n=4) of groundwaters from lavas and tuffs and from intrusive igneous rocks, which were combined into a single group (termed ‘Other’ in the figure captions in this report). Further, three of the groundwater samples from Ordovician and Silurian strata were mineralised and because their water quality was so obviously different from the rest they have been separated into their own group (termed ‘Mineralised’ in this report).

The distribution of many trace elements in groundwater is closer to being log-normally distributed rather than normally distributed and so trace element data were generally plotted on a log scale. This meant that the occasional high outlier did not cause the scaling to obscure the low concentration data on boxplots for trace elements. For some other parameters, such as Eh (redox status), zero or negative values are possible and no log scaling was used in these cases. Values for pH are already log transformed, and therefore no log scaling of this parameter was warranted. For most major ions, linear plots were used.

4.2 ACIDITY, REDOX AND THE MAJOR IONS

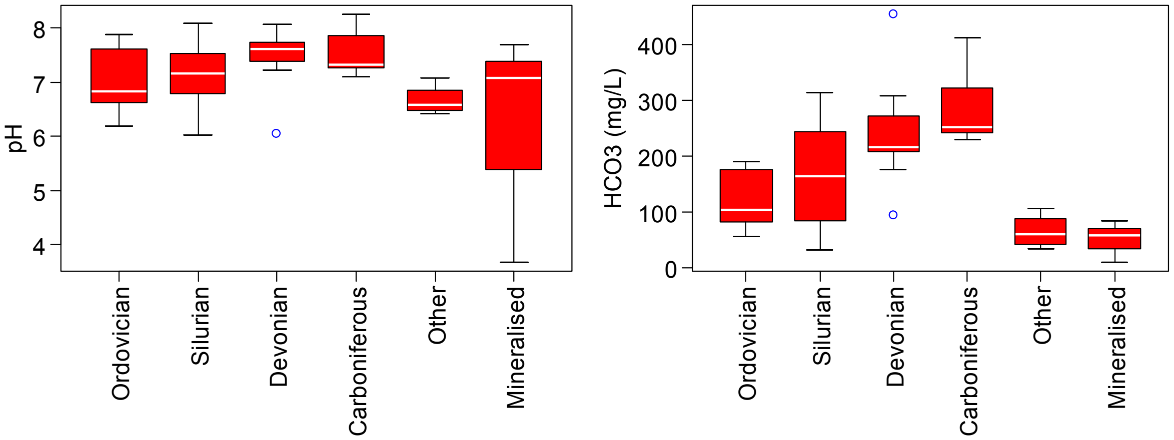
The pH, Eh and the concentration of the four major cations (Na^+, K^+, Ca^{2+} and Mg^{2+}) and four major anions (HCO_3^-, Cl^-, NO_3^-, SO_4^{2-}) together define the basic hydrogeochemical nature of a groundwater. They reflect the chemical composition of the rainfall (Section 1.6) and other surface inputs to the aquifer, outputs in the form of evaporation, and subsequent reaction of the groundwater with the aquifer mineral matrix.

In areas where the surface inputs are relatively small and nearly constant, the spatial variation in groundwater quality must largely reflect the variation in geology. On the other hand, for elements where the contribution from the geology is uniformly low, as with nitrate, the variations largely reflect variations in the inputs – in this case, from agriculture.

4.2.1 pH and alkalinity

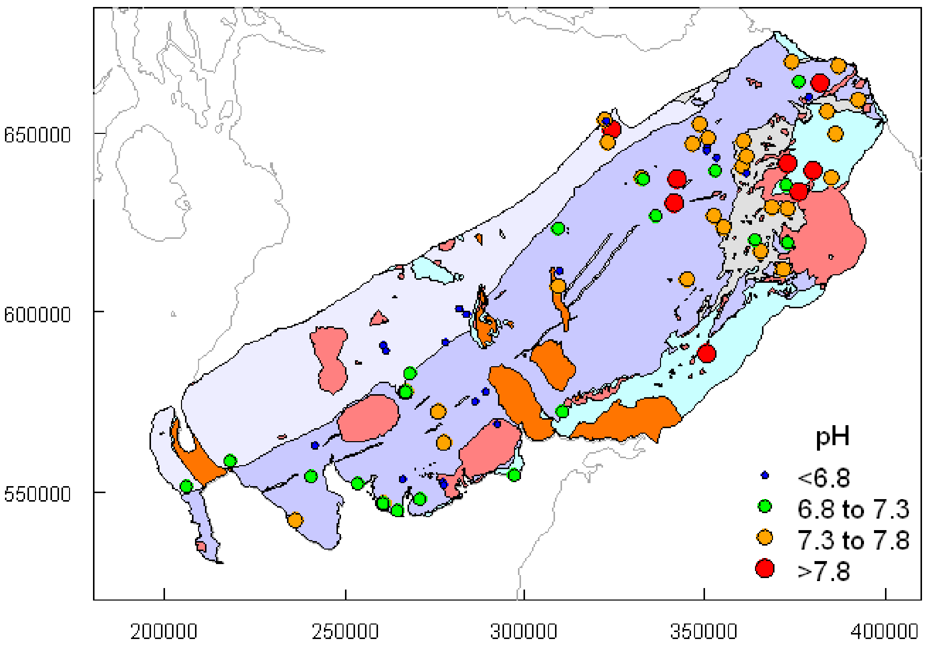
Most of the groundwater pH values in the area are in the near-neutral range (6.5-8.5), which is typical of UK groundwaters. Groundwaters from Lower Palaeozoic (Ordovician and Silurian) strata tend to have a slightly lower pH than groundwaters from the Devonian sandstones and Carboniferous sandstones and limestones (Figures 17 and 18). Groundwaters from igneous aquifers (‘Other’ in Figure 17) and from mineralised rock strata within the Lower Palaeozoic were more acidic, with occasional pH values below 6.5. The lowest pH found was 3.68 at Hartfell Spa near Moffat, a mineralised groundwater from the Ordovician Moffat Shale Group (Section 1.4.3).

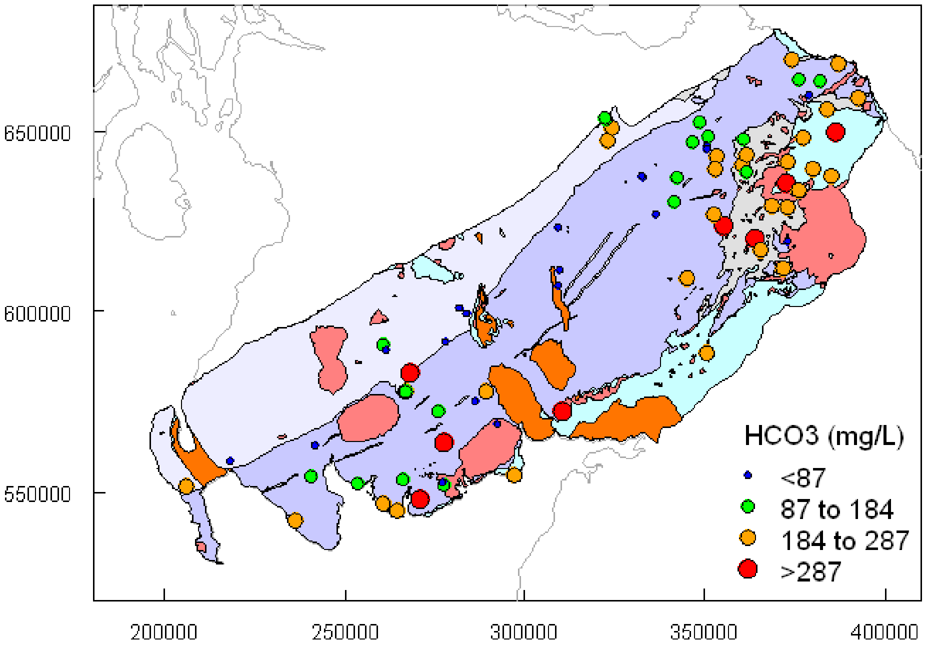
Similar trends are seen in bicarbonate alkalinity, with alkalinities of 100–250 mg HCO_3/l for Ordovician and Silurian groundwaters, 200–320 mg HCO_3/l for Devonian and Carboniferous groundwaters and <100 mg HCO_3/l for igneous and mineralised groundwaters. In general, groundwaters have greater alkalinities than surface waters (Section 1.5.2) because of the greater time that the percolating water has for reaction with rock carbonate.



The number of samples in each category is given in Table 2.

Figure 17 Boxplots showing the distribution of pH and alkalinity (as HCO_3) in groundwaters in aquifers across southern Scotland.





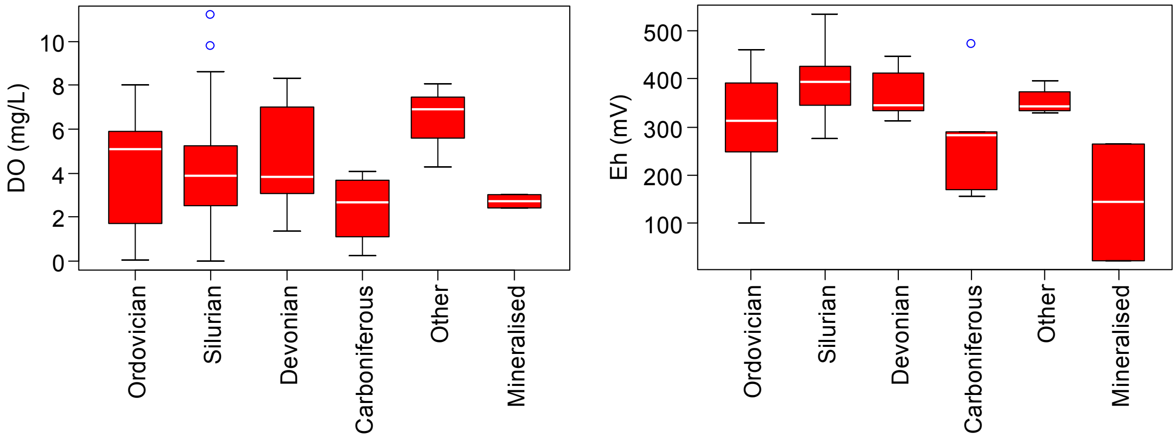
For key to geology see Figure 5.

Figure 18 Maps showing the spatial distribution of pH and alkalinity (as HCO_3) in groundwater across southern Scotland.

4.2.2 Dissolved oxygen and Eh

Most of the groundwaters in the study area are oxidising, with dissolved oxygen concentrations in the range 1–7 mg/l and a redox potential (Eh) greater than 300 mV. The saturated solubility of DO at 10°C is about 11 mg/l so percent saturations range up to about 70%. Only sample 70, from the Silurian aquifer, had a DO concentration (0.1 mg/l) of less than 1 mg/l and an Eh (277 mV) of less than 300 mV suggesting that it was mildly anaerobic. This is confirmed by its low nitrate concentration (<0.1 mg/l NO_3-N). However, the low Fe concentration found for this sample (<0.01 mg/l) suggests that it is not strongly reducing.

Overall, the redox status of the groundwaters did not appear to vary strongly with the geology – the only observation that might be made is that groundwaters from the Carboniferous strata tended to be slightly less oxidising than the other groundwaters. The mineralised springs, however, do indicate reducing conditions. The difficulty in monitoring wellhead chemistry at the sites may account for the presence of DO in the samples.



The 'Other' category refers to igneous aquifers. The number of samples in each category is given in Table 2.

Figure 19 Boxplots showing the distribution of dissolved oxygen (DO) and redox potential (Eh) in groundwaters in aquifers across southern Scotland.

4.2.3 Alkali metal and alkaline earth major elements

Concentrations of the major cations are often quite low, reflecting the 'hard rock' environment from which they have been derived and the relatively high rainfall of the area. Box plots are shown in Figure 20 and maps in Figure 21.

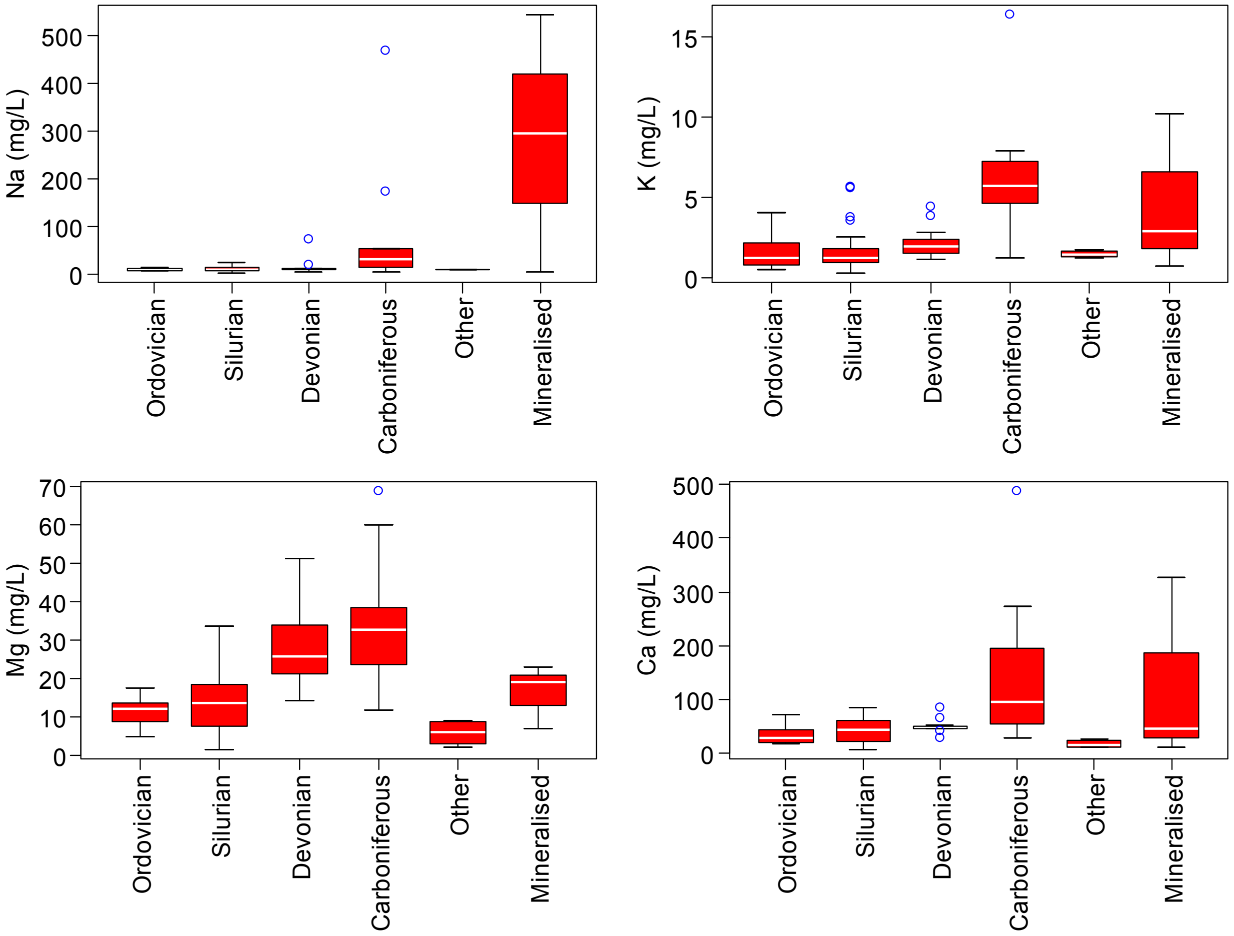
With median concentrations of Na on the order of 10 mg/l for groundwaters derived from the older rocks (Ordovician, Silurian and Devonian) and with an estimated rainfall contribution of approximately 4 mg/l (after evaporation), it is clear that the rainfall has made a substantial contribution to the Na in many of these groundwaters. Much of this will have been ultimately derived from seawater. In the Carboniferous strata in the Tweed catchment to the east of the area, Na concentrations are greater and it is likely that additional contributions will have been derived from the weathering of feldspars in the sandstone facies.

Potassium concentrations generally follow those of sodium with a relative enrichment in the Carboniferous sediments (5–10 mg/l) and low concentrations (1–2 mg/l) in the Palaeozoic strata.

Calcium concentrations are lowest in igneous and Ordovician groundwaters (15–40 mg/l) and highest in the Carboniferous limestone groundwaters (50–200 mg/l). There were several very highly mineralised samples with Ca concentrations greater than 200 mg/l. These were confined to the Carboniferous limestone and St Ronan's Spring (mineralised Silurian). The highest Ca concentration (487 mg/l) was in sample 29, from a deep borehole in the Inverclyde Group of the Carboniferous aquifer in the east of the study area, near Berwick on Tweed.

The Ca concentration broadly reflects the absence or presence of calcite (calcium carbonate) in the aquifer rock. Calcite is readily dissolved by CO_2-charged percolating groundwater releasing Ca and generating carbonate alkalinity. This distinction can be seen from the variation in calcite saturation index (SI_c). This was calculated using the `PHREEQC` geochemical speciation program and is based primarily on the *in situ* pH, Ca and HCO_3^- concentrations, and temperature of the groundwater sample. Values of the saturation index of less than zero indicate undersaturation with respect to calcite, and for values less than -0.3 are a good sign of the absence of calcite. Values of zero or greater than zero indicate saturation or supersaturation and the possible presence of the mineral.

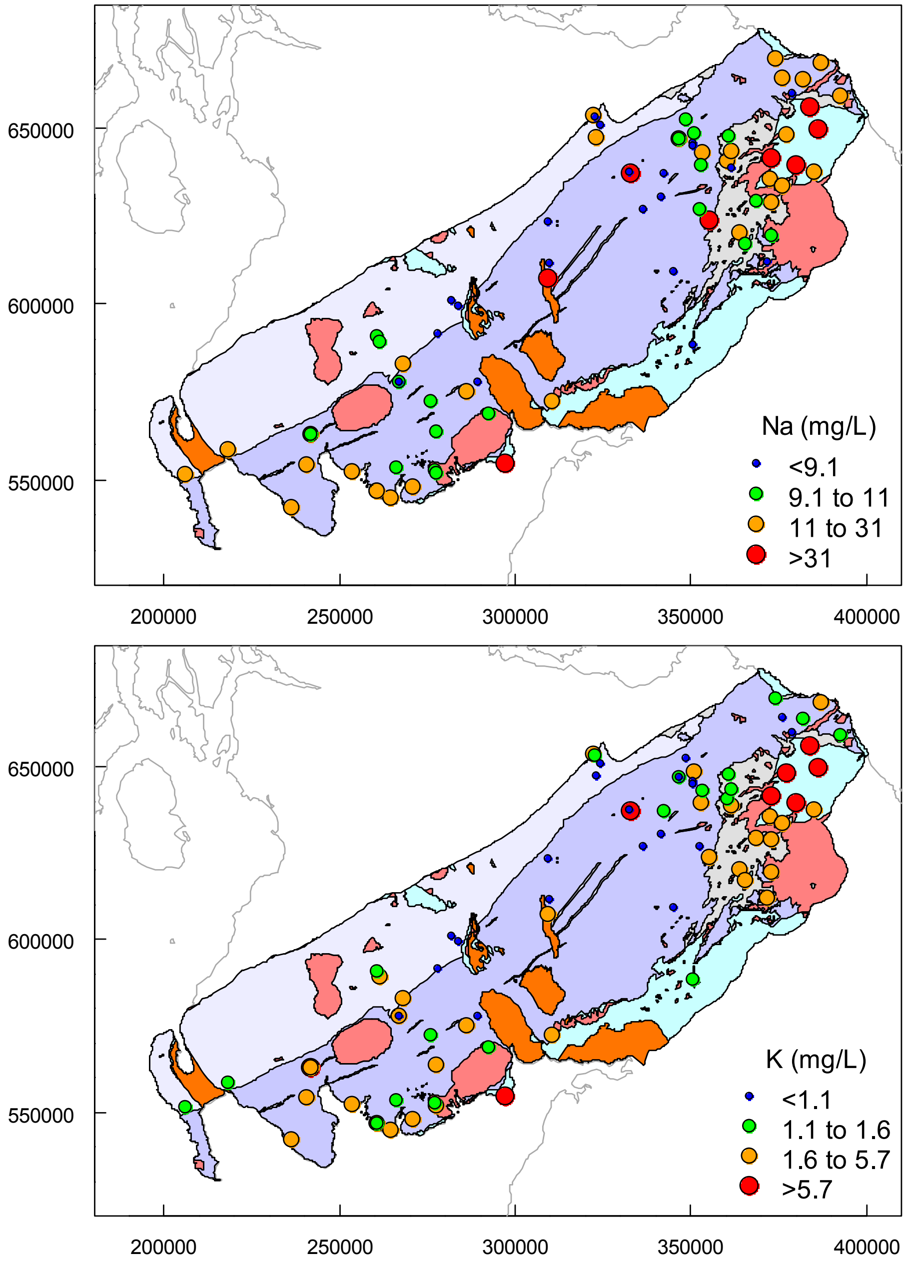
Values of the SI_c for groundwaters from the Ordovician, Siluran and igneous categories (including the mineralised beds) suggest undersaturation and the absence of calcite (Figures 23 and 24). This concurs with the known mineralogy of these rocks. Groundwater from the Devonian and Carboniferous strata are generally saturated or supersaturated and indicate the presence of calcite either as a major (Carboniferous limestone) or minor component (calcite sediment in Devonian sandstones). This is also demonstrated by the map of the spatial distribution of SI_c (Figure 24).



The 'Other' category refers to igneous aquifers. The number of samples in each category is given in Table 2.

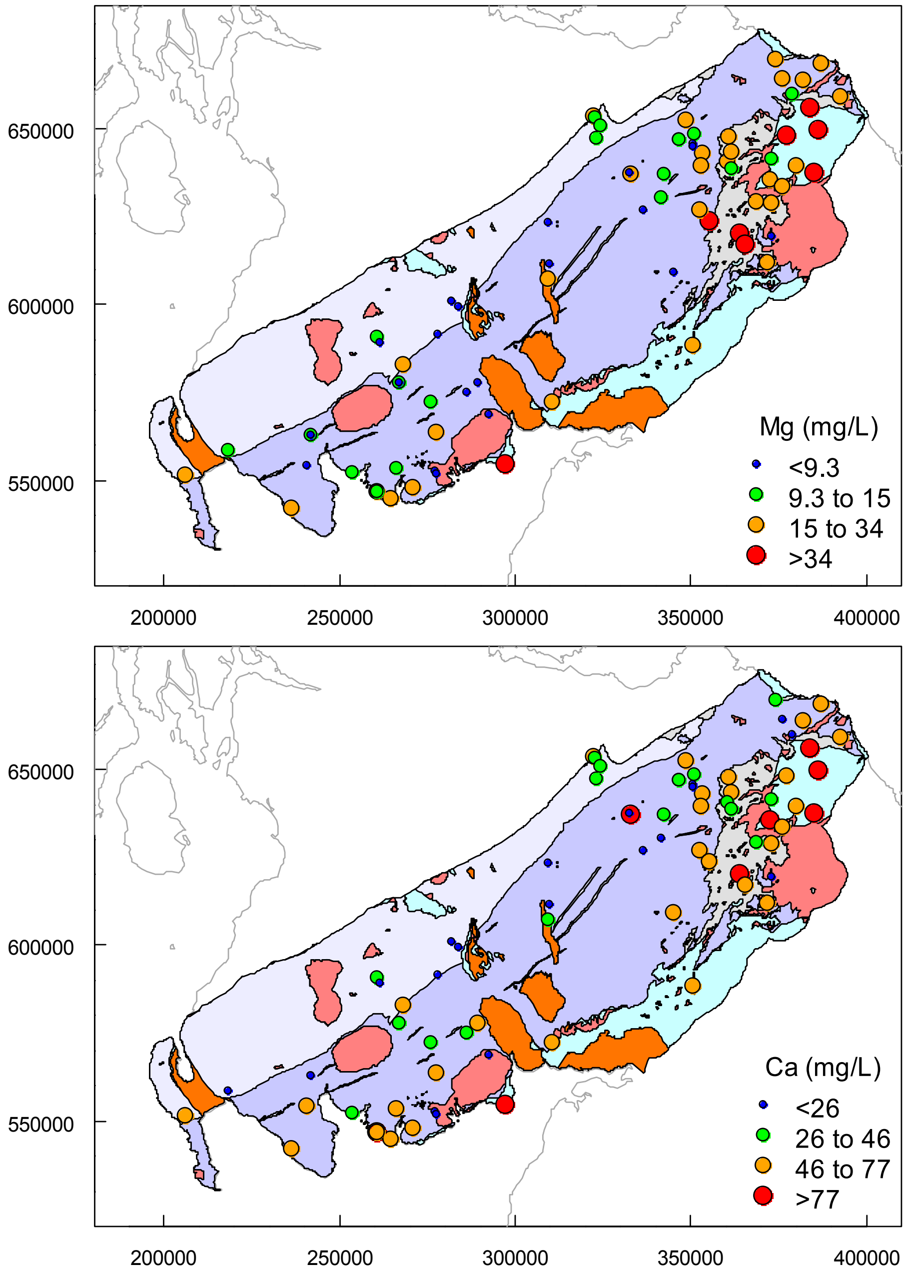
Figure 20 Boxplots showing the distribution of major cations (sodium, potassium, magnesium and calcium) in groundwaters in aquifers across southern Scotland.

A value greater than zero indicates saturation or supersaturation suggesting the presence of calcite in the aquifer rocks while a value of less than zero indicates undersaturation and probable absence of calcite.



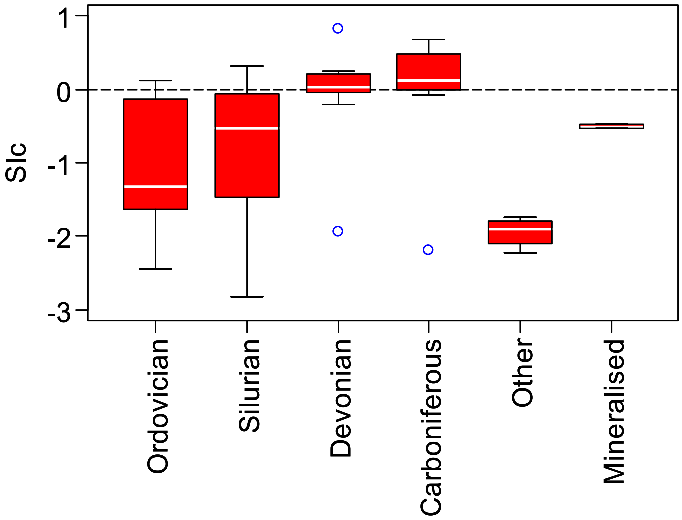
For key to geology see Figure 5.

Figure 21 Maps showing the spatial distribution of two of the four major cations (sodium and potassium) in groundwaters across southern Scotland.



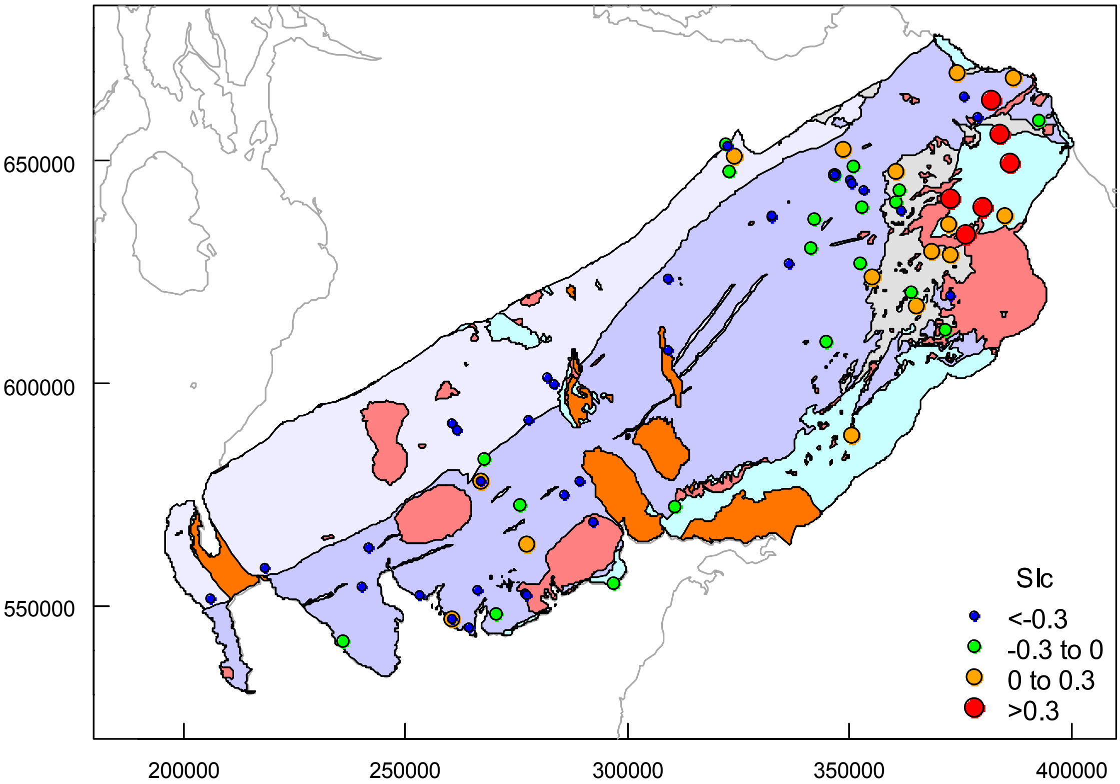
For key to geology see Figure 5.

Figure 22 Maps showing the spatial distribution of two of the four major cations (magnesium and calcium) in groundwaters across southern Scotland.



The 'Other' category refers to igneous aquifers. The number of samples in each category is given in Table 2.

Figure 23 Boxplot showing the distribution of calculated calcite mineral saturation indices (SI_c) in groundwaters in aquifers across southern Scotland.



For key to geology see Figure 5.

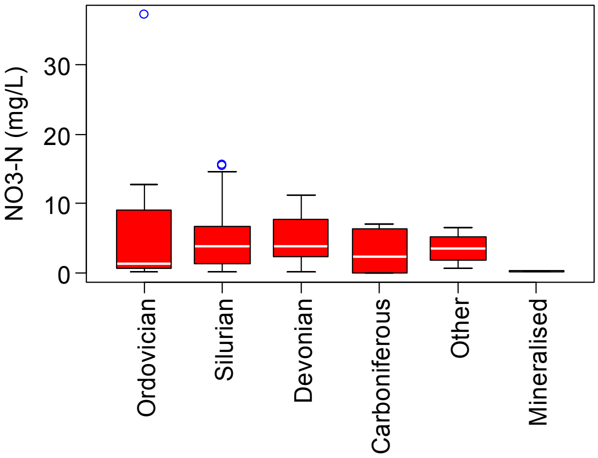
Figure 24 Map showing the spatial distribution of the calcite saturation index (SIc) for the sampled groundwaters across southern Scotland.

4.2.4 Chloride, sulphate and nitrate

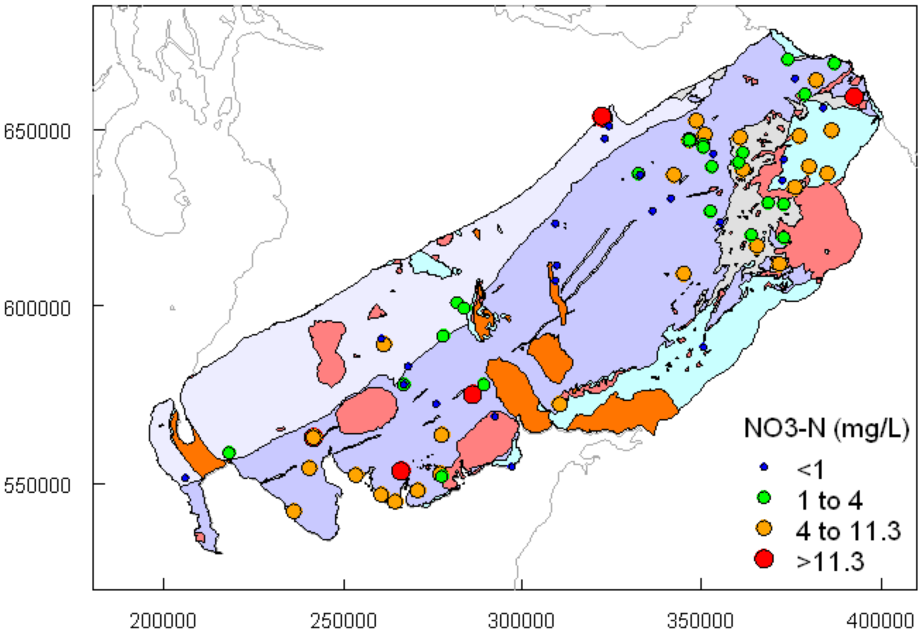
Chloride and sulphate concentrations are generally low and reflect inputs from rainfall and to a lesser extent from local sources of pollution, including fertilisers (Figure 26). Carboniferous groundwaters tend to have the largest concentrations of Cl and SO_4, possibly reflecting a contribution from the mudstones and shales. The mineralised waters from St Ronan's Sulphur Spring and Moffat Well have very high Cl concentrations (>500 mg/l), whereas the Hartfell Spa has a low Cl but high SO_4 concentration.

Nitrate concentrations were mostly low, with median concentrations less than 5 mg/l NO_3-N in all the aquifer groups (Figure 25), and most concentrations less than the drinking water limit of 11.3 mg/l NO_3-N (50 mg/l NO_3). There were six exceedances: the highest (sample 26) was 37 mg/l NO_3-N, and clearly indicates pollution. The surrounding land use is poultry farming, but groundwater from a second (newer) borehole at this site had a much lower nitrate concentration (12 mg/l NO_3-N) – although this still exceeds the drinking water limit.

The data were analysed in terms of land use based on the 200 m resolution land use classification of each site (Figure 27). There is not a clear distinction between the land use types, although agricultural land uses gave somewhat higher nitrate concentrations compared with non-agricultural land (woodland, semi-natural, buildings, recreational). The highest median nitrate concentrations were found beneath land used for rearing dairy, pigs and poultry (DPP). The depth of the groundwater source was also considered as a possible variable of significance but stratification of the data in this way does not show any consistent differences (Figure 28).



The ‘Other’ category refers to igneous aquifers. The number of samples in each category is given in Table 2.



For key to geology see Figure 5.

Figure 25 Boxplot and map showing the distribution of nitrate concentrations in groundwaters in aquifers across southern Scotland.

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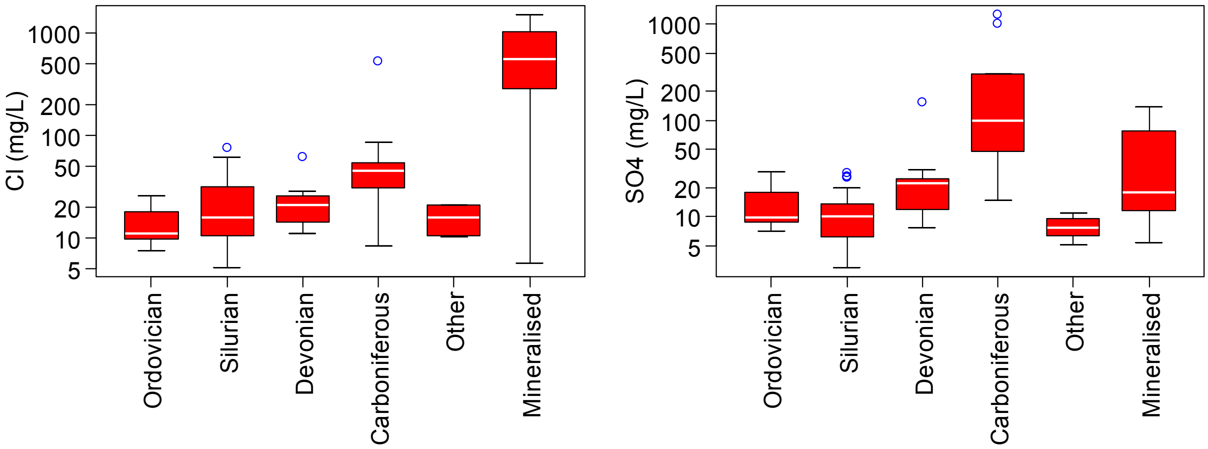
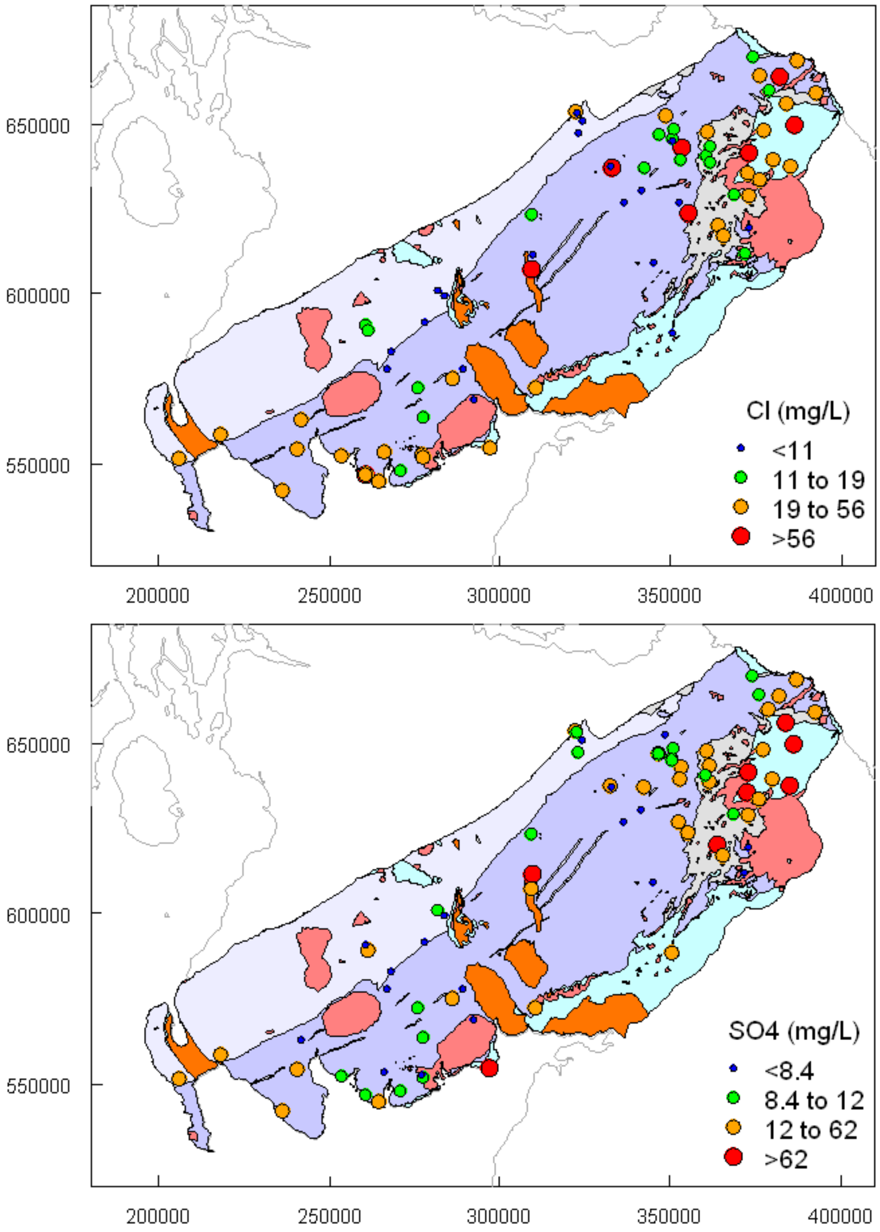
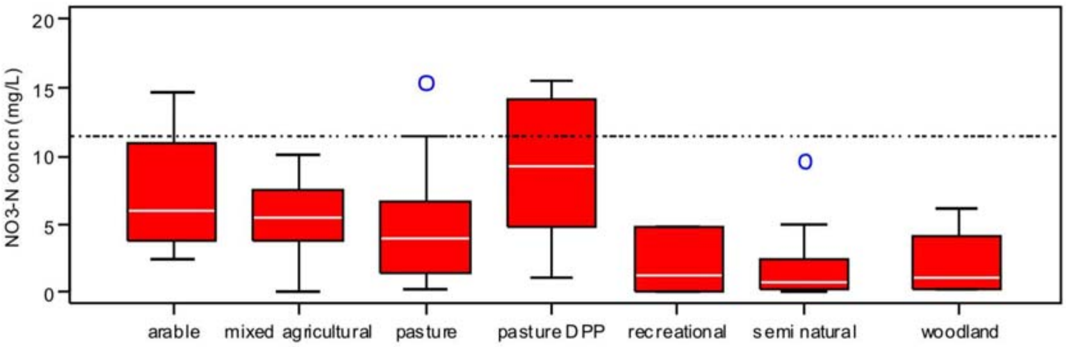


The 'Other' category refers to igneous aquifers. The number of samples in each category is given in Table 2.



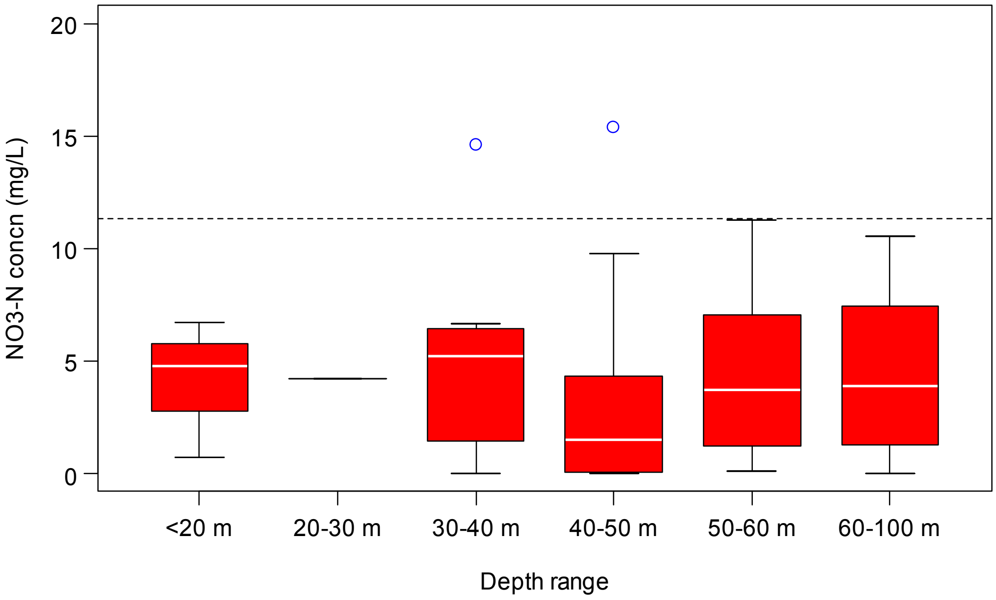
For key to geology see Figure 5.

Figure 26 Boxplots and maps showing the distribution of chloride and sulphate concentrations in groundwater in aquifers in southern Scotland.



The number of samples in each category is given in Table 2. The drinking water limit for NO_3-N (11.3 mg/l) is shown as a horizontal dashed line.

Figure 27 Variations of nitrate concentrations in groundwater with land use type, based on land use maps and field observations of the 200 m surrounding the groundwater source.



n=23

Figure 28 Variation in nitrate concentrations in groundwaters in southern Scotland with measured source depth.

4.3 IRON AND MANGANESE

4.3.1 Iron

With the exception of the mineralised or partially mineralised samples, Fe concentrations were mostly low and often below the detection limit (0.01 mg/l). This is characteristic of oxidising waters. The median concentration in the Carboniferous waters (0.02 mg/l) was slightly greater than for the other non-mineralised waters. Other than the mineralised waters, there was not a strong correlation between Fe and Mn concentrations. Maps and boxplots are shown in Figure 29.

4.3.2 Manganese

While median Mn concentrations were mostly below 50 µg/l (the drinking water standard), there were a significant number above this value. This included the mineralised and partially mineralised waters. Although the median concentration was greater in the Ordovician and Carboniferous groundwaters than in the Silurian groundwaters, there were more outliers in the Silurian groundwaters. Maps and boxplots are shown in Figure 29.

4.4 SILICON AND MINOR ELEMENTS

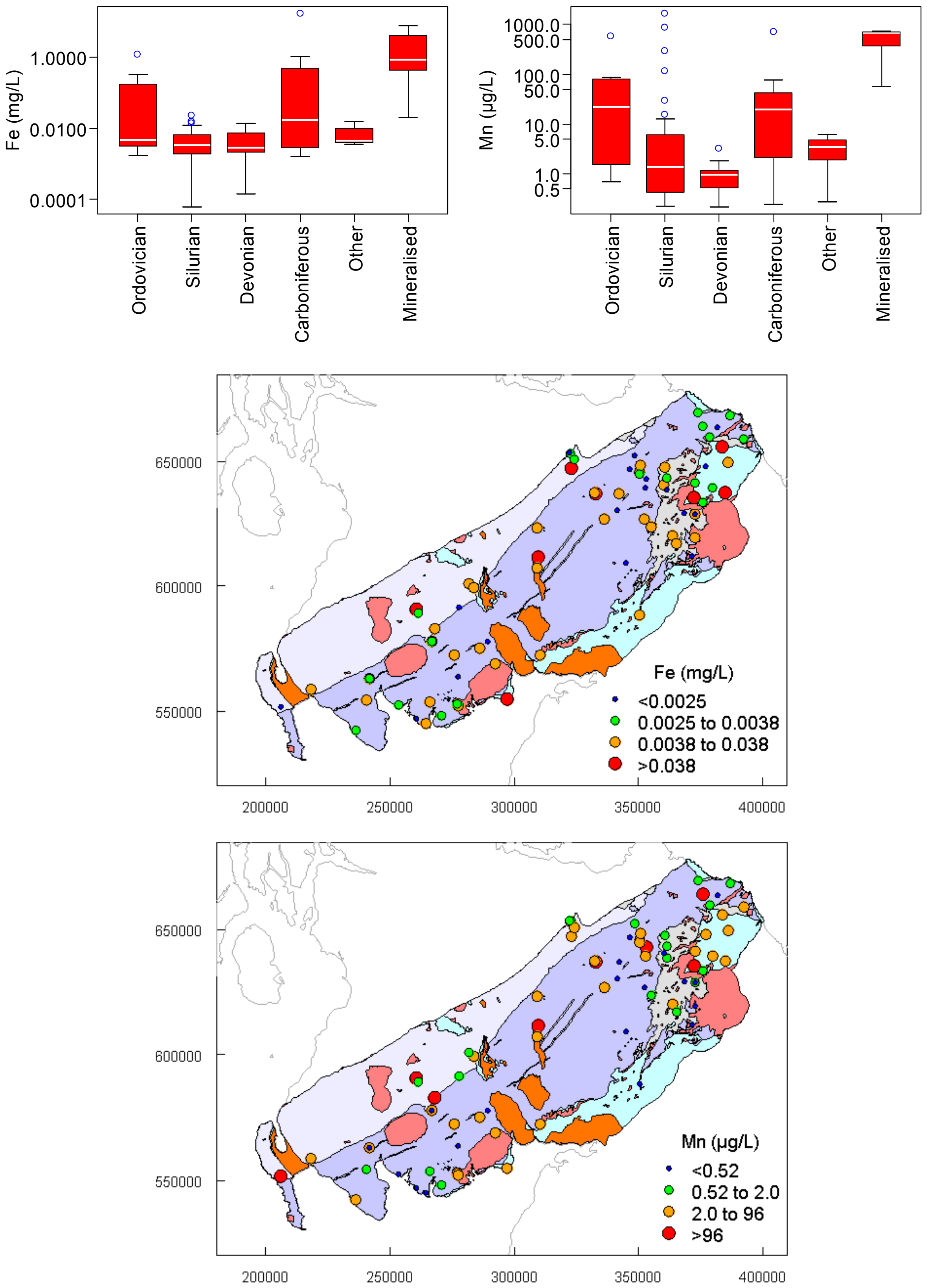
4.4.1 Silicon

There was relatively little variation in Si concentrations, with most values falling in the range 4 to 7 mg/l. This reflects the ubiquity of quartz or its more soluble polymorphs such as cristobalite. Si concentrations are close to saturation or slightly supersaturated with respect to quartz.

Unusually high Si concentrations were found in the mineralised Hartfell Spa sample (20 mg/l) and the partially mineralised water from sample 31, in the Carboniferous aquifer.

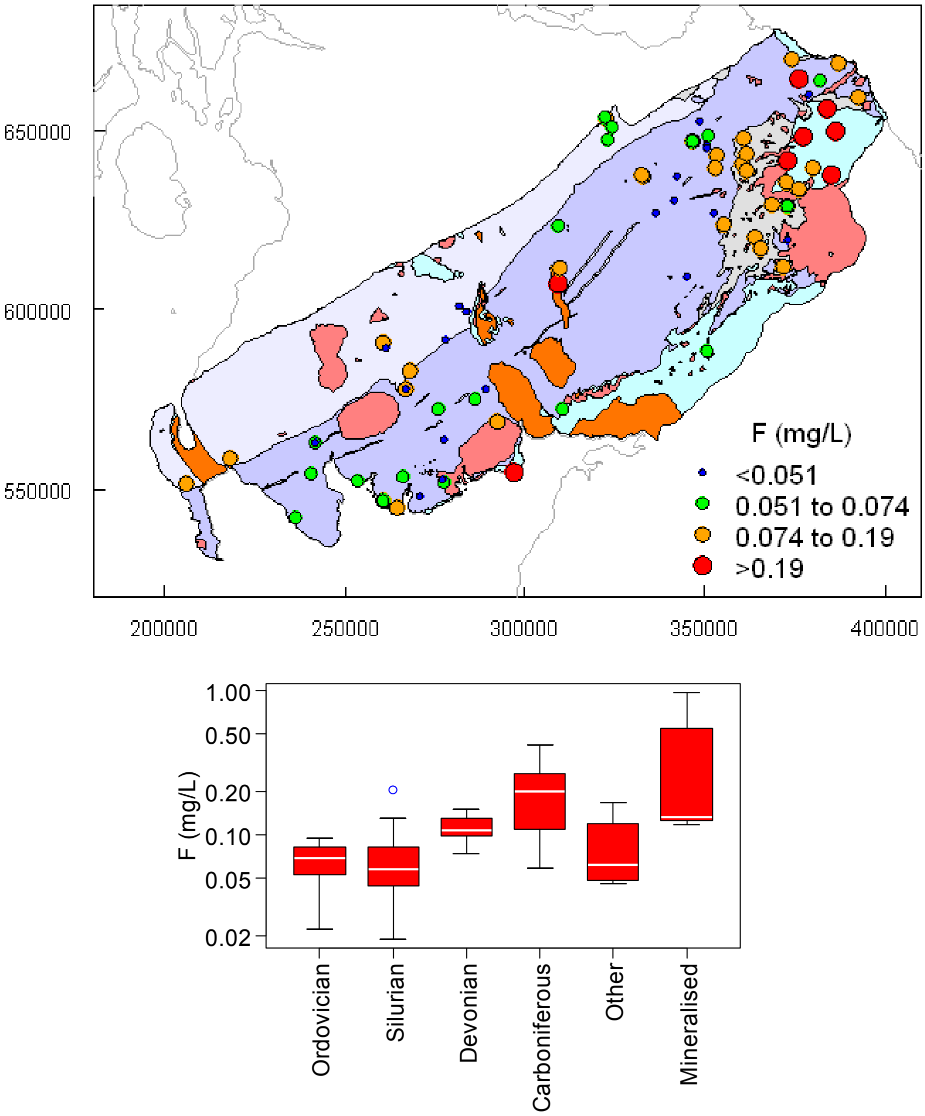
4.4.2 Fluoride

Fluoride concentrations are low throughout the study area, with median concentrations less than 0.2 mg/l, and a maximum concentration of 1.0 mg/l in Moffat Well (Figure 30). Concentrations tend to be greatest in groundwaters from Carboniferous aquifers in the east of the study area.



The 'Other' category refers to igneous aquifers. The number of samples in each category is given in Table 2. For key to geology see Figure 5.

Figure 29 Boxplots and maps showing the distribution of iron and manganese concentrations in groundwater in aquifers across southern Scotland.



The 'Other' category refers to igneous aquifers. The number of samples in each category is given in Table 2. For key to geology see Figure 5.

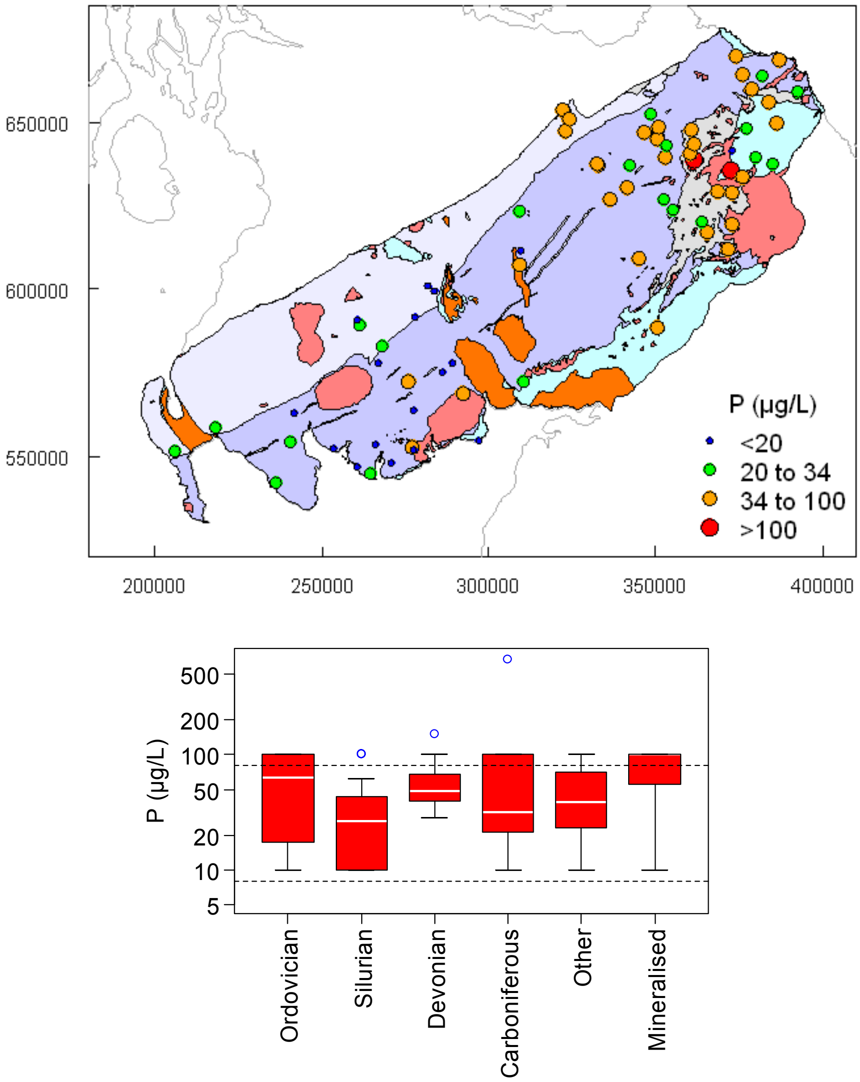
Figure 30 Boxplot and map showing the distribution of fluoride concentrations in groundwater in aquifers across southern Scotland.

4.4.3 Phosphorus

Phosphorus (phosphate) was measured by ion chromatography, and both ICP-AES and ICP-MS (total P). However, many of the results were below the method detection limits. The most sensitive method was ICP-MS, which usually had a detection limit of 20 µg P/l (however, for some of the additional samples it was ten times greater than this value due to the analysis methods). The ICP-MS (total P) results are used here; however, 20 out of 78 values (26%) were censored. More sensitive analytical methods (e.g. colorimetry) would be required to quantify P concentrations of less than 20 µg P/l. While 20 µg P/l is not exceptionally high for many groundwaters, both within and outwith the current study area, it is greater than the 8 µg P/l management limit set by SEPA for oligotrophic surface waters, (25 and 80 µg P/l limits apply to mesotrophic and eutrophic surface waters, respectively, based on annual geometric mean concentrations).

The phosphate concentrations show an overall median of 29 µg P/l (Figure 31). Maximum concentrations were close to or below 100 µg P/l for most of the formations. A single high concentration of 680 µg P/l was found in sample 31, in the Carboniferous aquifer in the east of the study area. This water is anomalous in several respects, including a very high Fe concentration (16 mg/l). It could be that some of this Fe was in particulate (oxidised) form and had adsorbed P attached to the particles. Phosphate is known to bind strongly to Fe-rich particles. Aside from the mineralised waters, which tended to be slightly higher in P concentration, there was little difference in P concentration between the various aquifer groups. Median P concentrations for each of the various groups tended to fall in the range 30-70 µg P/l, which is in the mesotrophic range for surface waters.

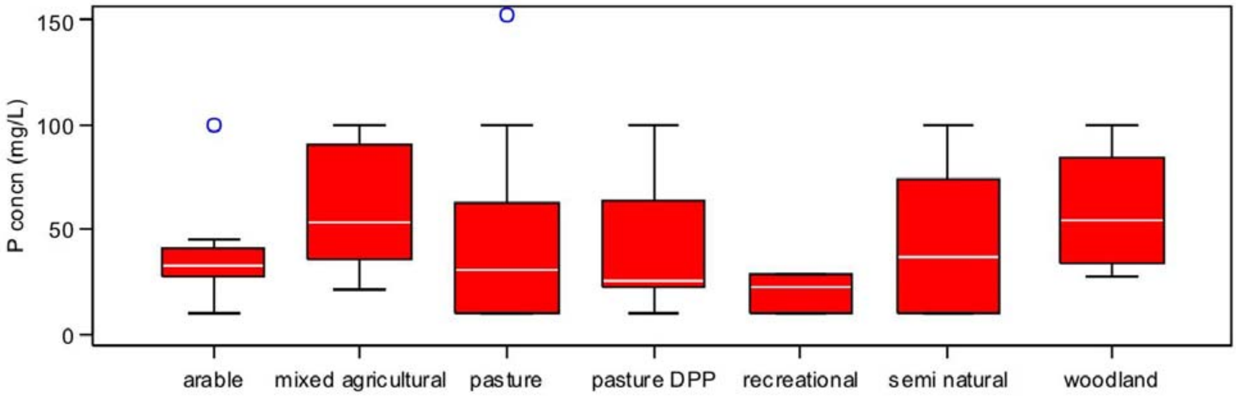
Somewhat surprisingly, P concentrations do not show any strong influence of land use (Figure 32) with no simple clear pattern emerging. This illustrates the complexity of P geochemistry and the important role that soil geochemistry plays in the mobilisation of P into groundwater.



The 'Other' category refers to igneous aquifers. The number of samples in each category is given in Table 2. For key to geology see Figure 5.

The horizontal dashed lines are positioned at 8 and 80 µg P/L which correspond to the SEPA management limits for P in oligotrophic and eutrophic surface water bodies, respectively.

Figure 31 Boxplot and map showing the distribution of phosphorus concentrations in groundwater in aquifers across southern Scotland.



The number of samples in each category is given in Table 2.

Figure 32 Variation of phosphorus concentrations in groundwater across southern Scotland with land use type, based on land use maps and field observations of the 200 m surrounding the groundwater source.

4.4.4 Boron

Boron concentrations are low (<30 µg/l) in many of the groundwaters and exceeded 200 µg/l only in some of the Carboniferous formations and the mineralised springs (Figure 33). The highest concentration was 980 µg/l in sample 29, from a deep borehole in the Carboniferous aquifer. This was an Al- and SO_4-rich groundwater and the elevated boron may be associated with the weathering of mudstones within the Carboniferous rocks or possible mixing with other mineralised waters.

4.4.5 Arsenic

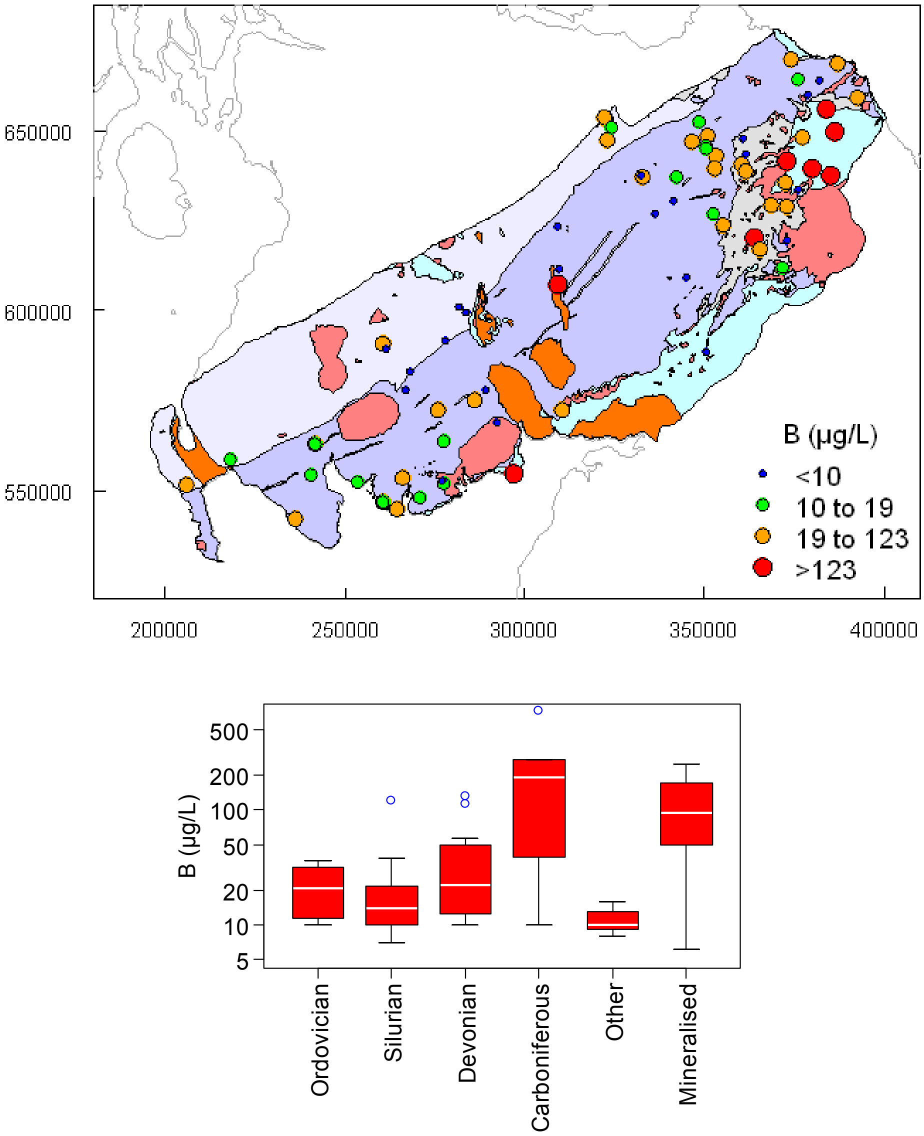
Concentrations of As were generally low, with median concentrations for the various geological groupings all below 2 µg/l and only two samples above the drinking water standard of 10 µg/l. These were sample 31 (37 µg/l) and sample 68 (16 µg/l). More than half of the samples (56%) were below the detection limit (0.5 µg/l). Concentrations appeared to be slightly greater in the mineralised groundwaters (Figure 34). The groundwaters from Silurian aquifers tended to contain more high outliers, especially in the west. This may reflect nearby mineralisation.

4.4.6 Uranium

Uranium concentrations were generally low, with median concentrations of less than 1 µg/l in all aquifer groups. Only a few outliers reached concentrations up to 10 µg/l. Igneous rocks (the ‘Other’ category in Figure 35) showed the widest range in U concentrations, but a similar median value to most other groups. Ordovician aquifers and mineralised springs showed the lowest median and overall concentrations.

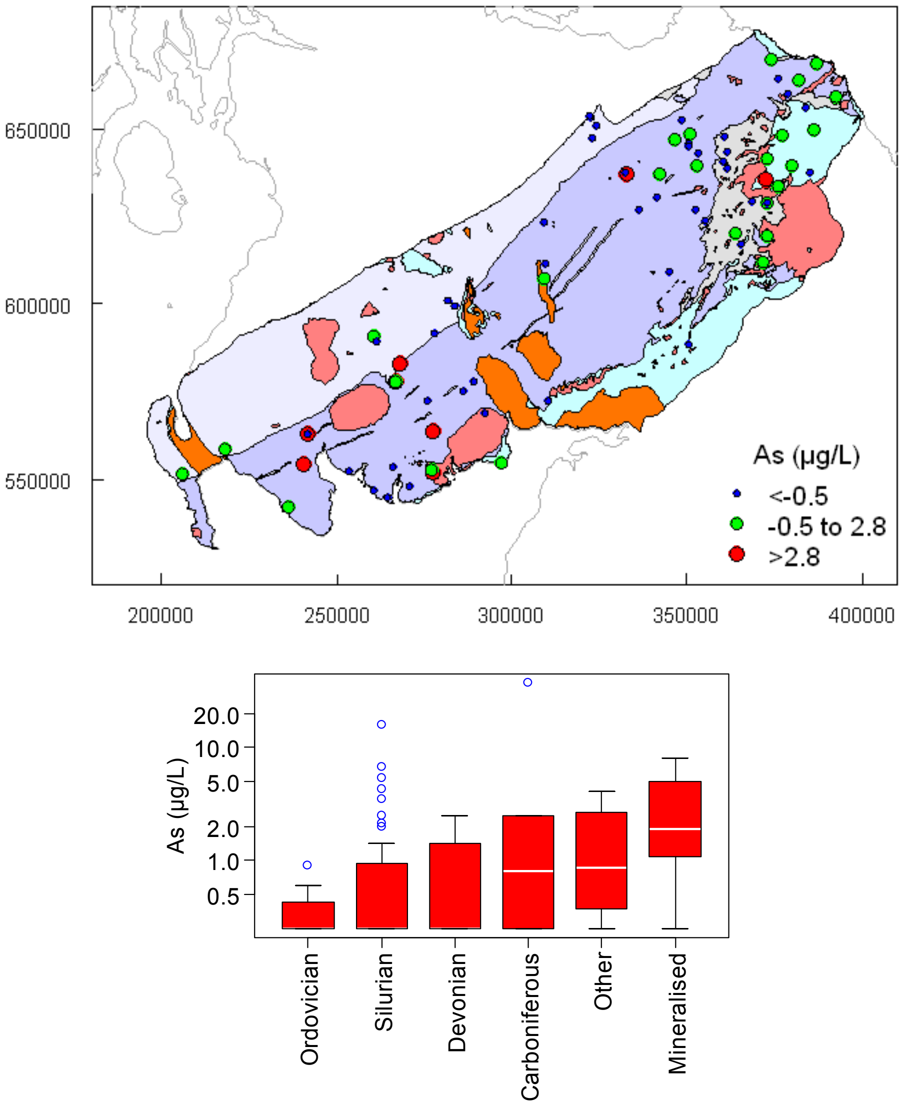
4.4.7 Molybdenum

Molybdenum concentrations are generally low (Figure 36). The median concentration is <0.1 µg/l and the maximum concentration is 36 µg/l, in sample 71 from a borehole in a major granite in the southwest of the study area (i.e., within the ‘Other’ category). Only ten of the groundwater samples showed a Mo concentration greater than 1 µg/l. The second highest concentration seen was 8 µg/l in sample 53, in the Carboniferous aquifer in the east of the study area. Concentrations in Carboniferous groundwaters tend to be slightly higher than in other aquifer groups. Igneous rocks showed the largest range in Mo concentrations.



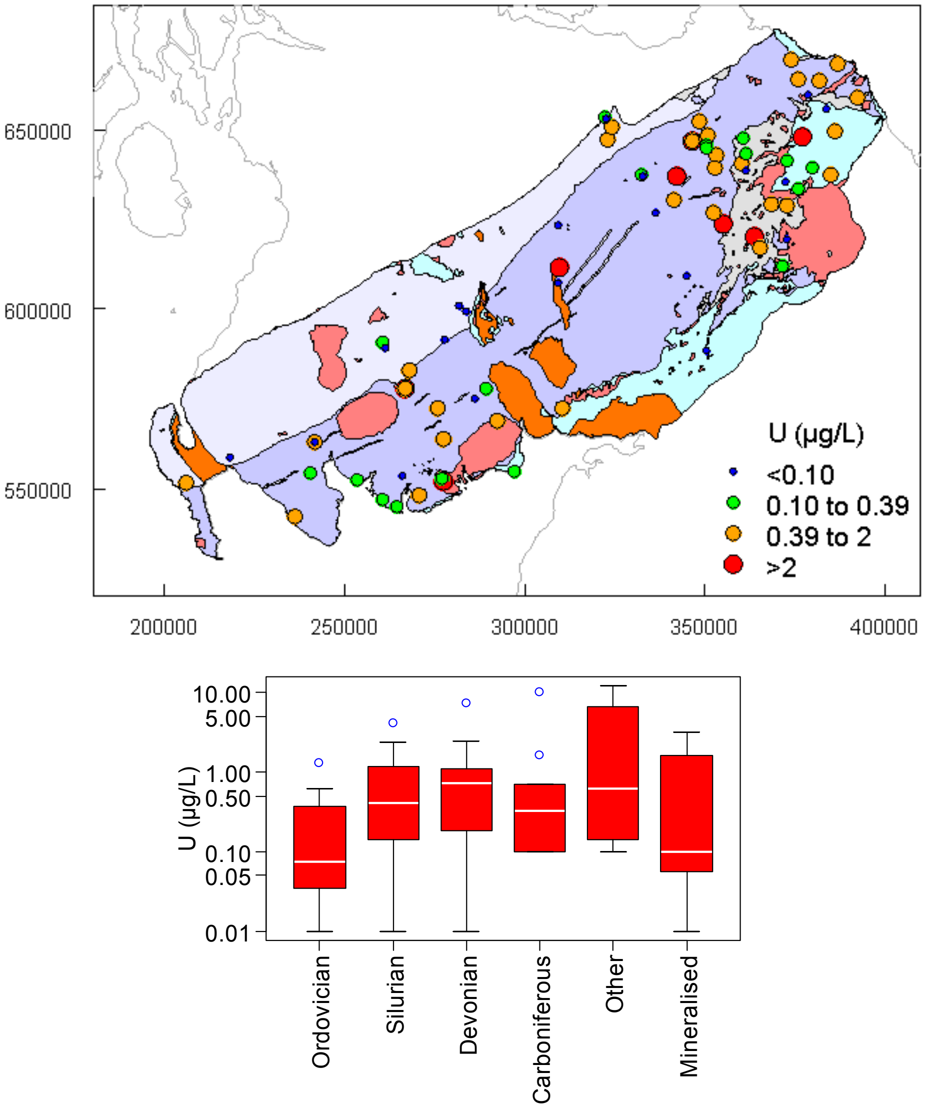
The 'Other' category refers to igneous aquifers. The number of samples in each category is given in Table 2. For key to geology see Figure 5.

Figure 33 Boxplot and map showing the distribution of boron concentrations in groundwaters in aquifers across southern Scotland.



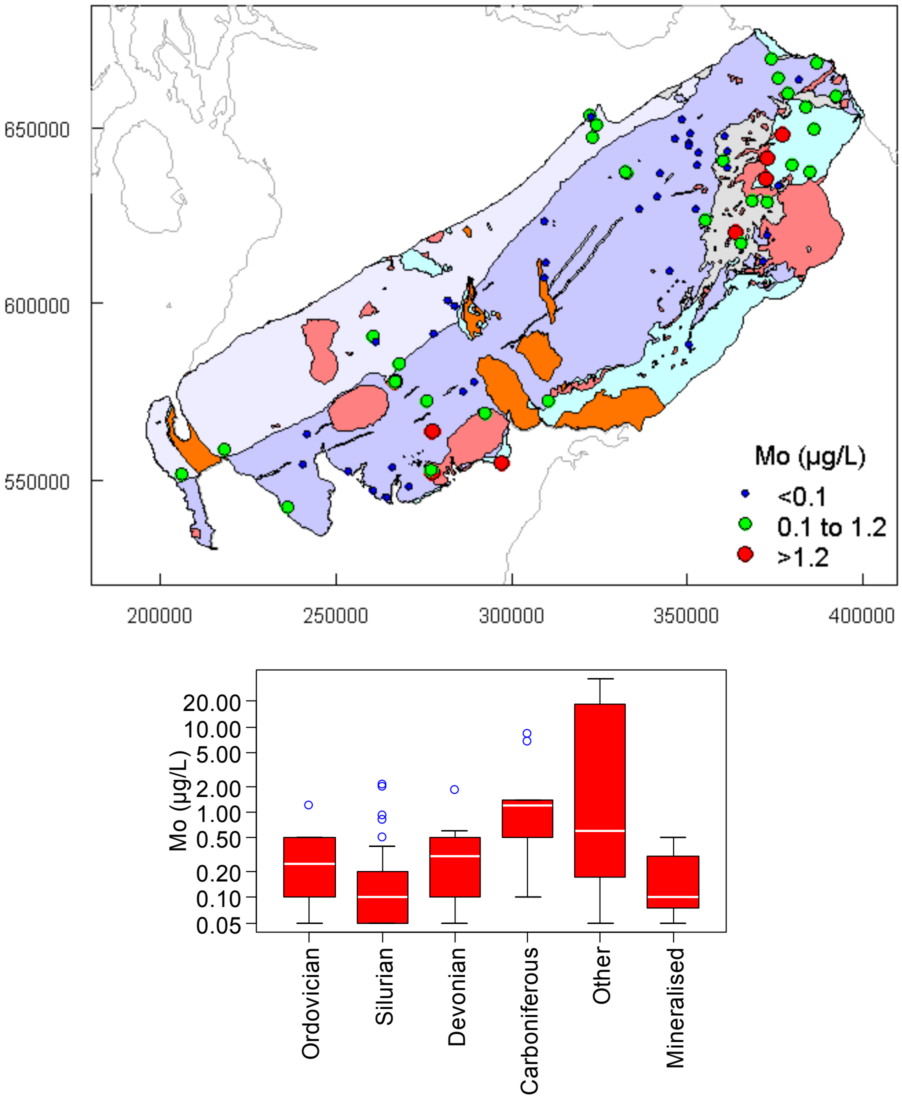
The 'Other' category refers to igneous aquifers. The number of samples in each category is given in Table 2. For key to geology see Figure 5.

Figure 34 Boxplot and map showing the distribution of arsenic concentrations in groundwater in aquifers across southern Scotland.



The ‘Other’ category refers to igneous aquifers. The number of samples in each category is given in Table 2. For key to geology see Figure 5.

Figure 35 Boxplot and map showing the distribution of uranium concentrations in groundwater in aquifers across southern Scotland.



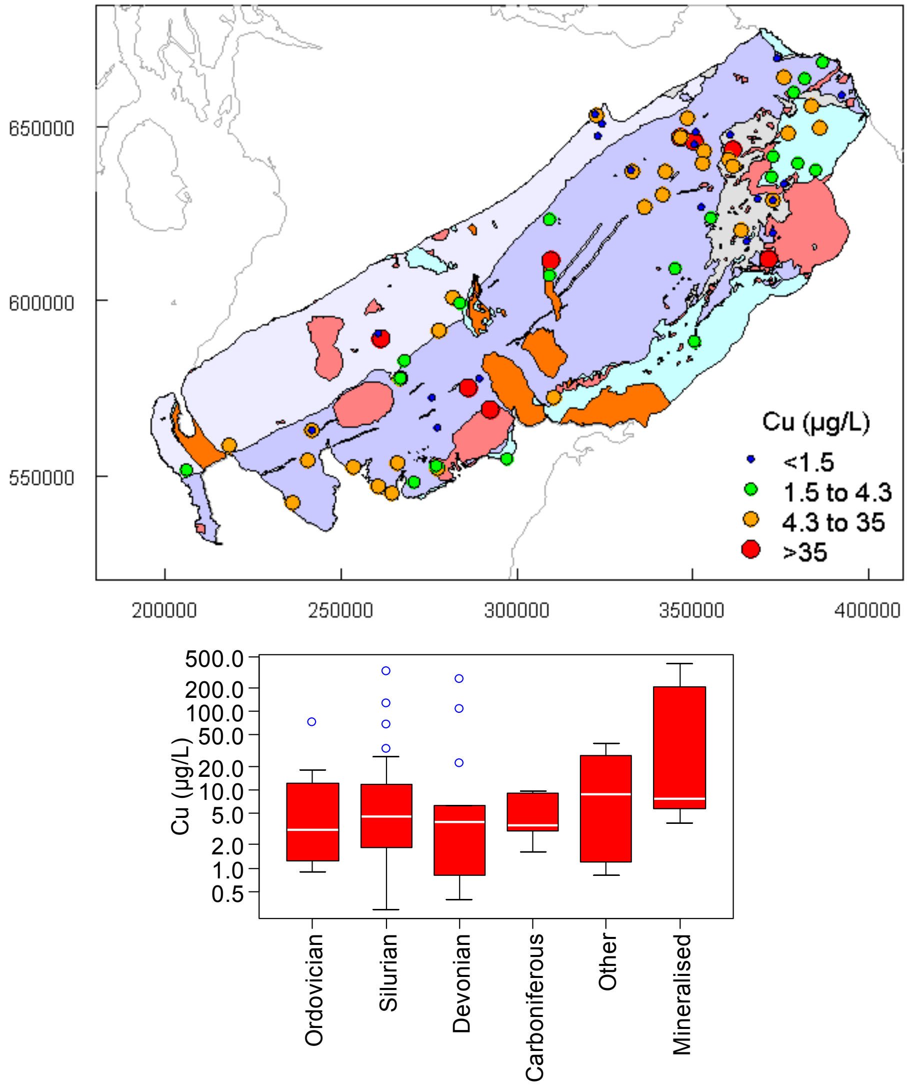
The 'Other' category refers to igneous aquifers. The number of samples in each category is given in Table 2. For key to geology see Figure 5.

Figure 36 Boxplot and map showing the distribution of molybdenum concentrations in groundwaters in aquifers across southern Scotland.

4.5 OTHER TRACE ELEMENTS

4.5.1 Copper

Most groundwaters have Cu concentrations of below 10 µg/l, but there are some significant outliers, with five samples containing more than 100 µg/l. This includes Hartfell Spa (401 µg/l) and sample 10, from a spring source in the Silurian aquifer (321 µg/l). However, the nearby sample 9, also from a spring in the Silurian aquifer, contained only 1 µg/l. This suggests the possibility of local Cu contamination from copper pipes carrying spring water to the sampling point some 300 m distant. A map and boxplot are shown in Figure 37.



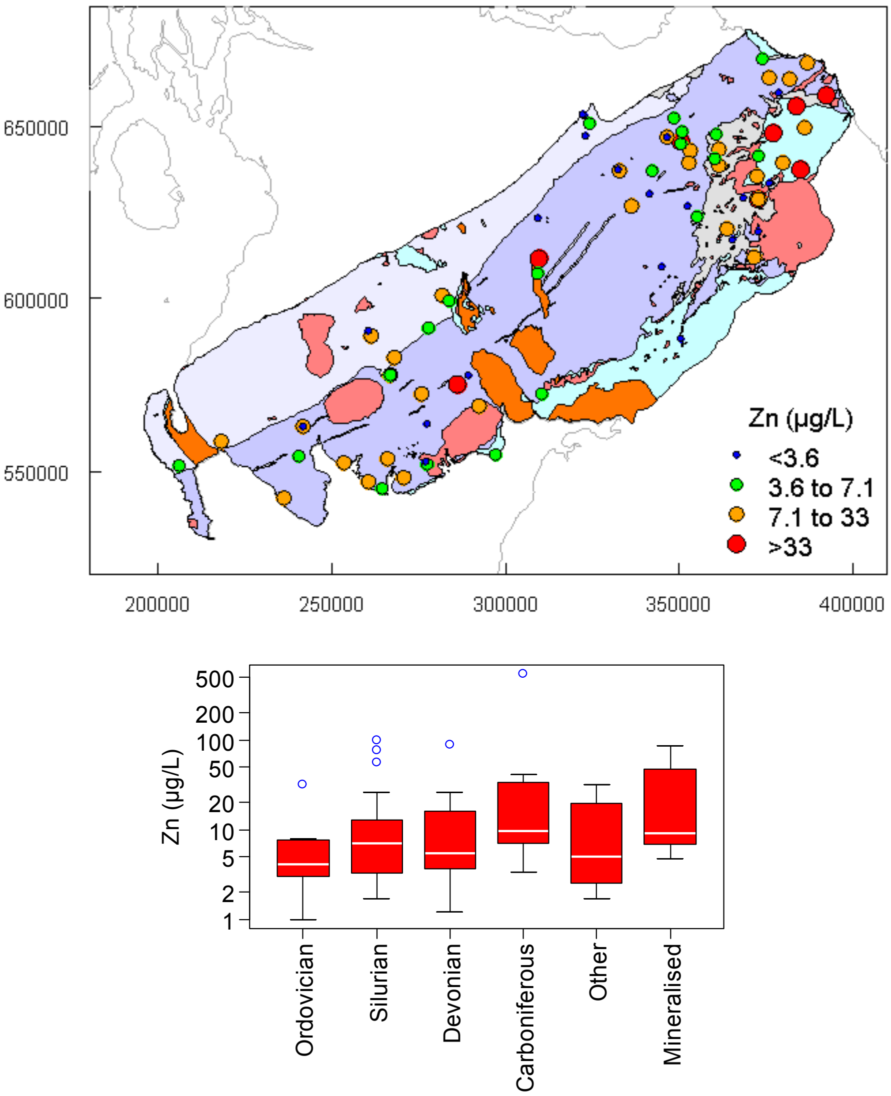
The 'Other' category refers to igneous aquifers. The number of samples in each category is given in Table 2. For key to geology see Figure 5.

Figure 37 Boxplot and map showing the distribution of copper concentrations in groundwaters in aquifers across southern Scotland.

4.5.2 Zinc and cadmium

Most of the groundwaters contain 2–50 µg/l Zn, with little difference between aquifer groups. Six sites showed more than 50 µg/l Zn. There is a zone in the east of the study area with relatively high Zn concentrations. The highest concentration (542 µg/l) was from sample 6, from a borehole in the Carboniferous aquifer. A map and boxplot of Zn concentrations are shown in Figure 38.

All but five groundwaters had Cd concentrations below the limit of detection (0.05 µg/l). The maximum concentration found (1.3 µg/l) was in sample 6 which, as noted above, also had the highest Zn concentration. There is usually a high correlation between Zn and Cd in waters and sediments. A Zn-Cd ratio of about 400 is typical of many natural waters; the ratio for sample 6 is 420.

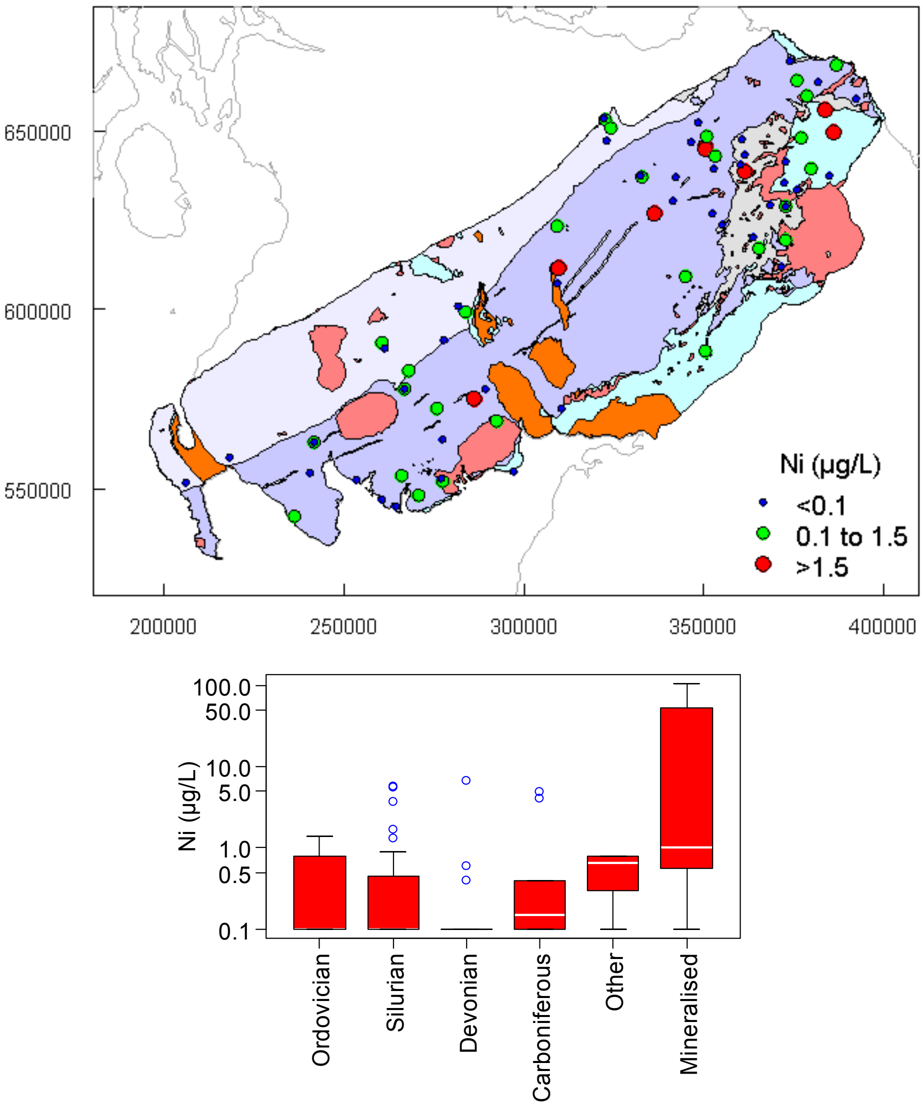


The ‘Other’ category refers to igneous aquifers. The number of samples in each category is given in Table 2. For key to geology see Figure 5.

Figure 38 Boxplot and map showing the distribution of zinc concentrations in groundwaters in aquifers across southern Scotland.

4.5.3 Nickel

The concentrations of Ni are very low, mostly less than 1 µg/l with outliers up to 7 µg/l. 43 (54%) sites contained less than the method detection limit (0.2 µg/l). Hartfell Spa had by far the highest concentration observed (106 µg/l). The next highest concentration was 7 µg/l. A map and boxplot are shown in Figure 39.



The ‘Other’ category refers to igneous aquifers. The number of samples in each category is given in Table 2. For key to geology see Figure 5.

Figure 39 Boxplot and map showing the distribution of nickel concentrations in groundwaters in aquifers across southern Scotland.

4.5.4 Rare earth elements

The lanthanide elements consist of the 15 elements lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb) and lutetium (Lu). Promethium is radioactive and does not exist naturally other than in minute quantities as a fission product.

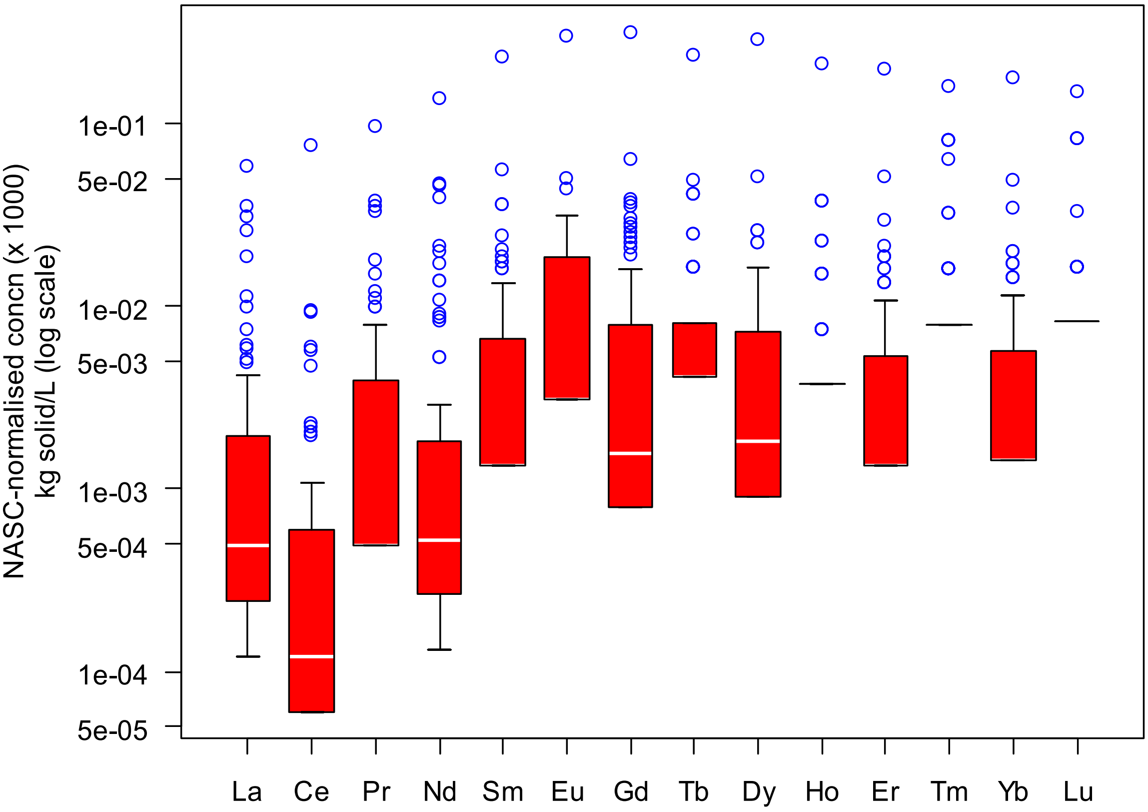
The relative concentrations of the various lanthanide elements follow a distinct pattern, with the most abundant element in nature usually Ce, followed by La. Most of the elements exist in the trivalent state and are most soluble under acidic conditions. Since most of the groundwaters in the study area are near neutral, concentrations of many of the REE are low, and often below the detection limit (s).

The greatest total concentration of REE was found at Hartfell Spa (sample 77) (22 µg/l). Sample 42, from the Silurian aquifer, contained 5 µg/l, and sample 27, from the Ordovician aquifer, contained 5 µg/l. The latter site is very close to the Southern Upland Fault at the northern edge of the study area. The high concentration at Hartfell Spa reflects its low pH (3.68) and is also reflected in its very high Al concentration (10,000 µg/l). The other two mineralized samples contained low concentrations of all REEs, in part reflecting their higher pH.

While most of the REEs remain in the +3 oxidation state, some can change under varying redox conditions. The most significant of these gives rise to a so-called 'cerium anomaly'. This can be positive (Ce concentration greater than expected from its neighbouring REEs) or negative (Ce concentration less than expected from its neighbouring REEs). In oxidising groundwaters, negative Ce anomalies are most common since Ce^{3+} is readily oxidised to Ce^{4+} and forms an insoluble Ce(IV) oxide.

Concentrations of the REEs in the groundwaters have been normalised to the North American Shale Composite (NASC) (Sholkovitz, 1988) to counteract the systematic variability in concentrations between REE with even and odd atomic numbers.

The normalised ratios were calculated for each element and for each sample and the distribution of values shown in a boxplot (Figure 40).



Median values are shown by white horizontal lines, except where 50% of the analyses were below the detection limit.

Figure 40 Boxplot showing the distribution of the concentrations of REEs normalised according to the NASC 'average' shale.

The median ratios show a negative Ce anomaly reflecting the generally oxidising nature of the groundwaters (Figure 40). There is a slight enhancement in the normalised concentrations of the heavy REE (HREE) (Eu–Lu) over the light REE (La–Sm). This is seen in the rising curve of the interquartile range as well as in the outliers. The largest outlier is for the Hartfell Spa sample, which shows the enrichment of HREE, albeit to a somewhat lesser extent than the median concentrations. Enrichment of the HREE is often due to the formation of soluble complexes, which tend to be more stable for the HREE. These complexes are most likely to be carbonate (but not for the acidic Hartfell Spa sample, where they are likely to be chloride or sulphate.

4.5.5 Other transition and heavy metals

Scandium concentrations were mostly close to or below the detection limit with the highest concentration at 6 µg/l in Hartfell Spa.

Titanium concentrations were all below the detection limit (<10 µg/l in most cases).

Vanadium concentrations were mostly <1 µg/l. There were relatively high concentrations in sample 65, (10 µg/l), from a borehole in the Silurian aquifer in the west of the study area, and in sample 54 (7 µg/l), from the Devonian aquifer in the east. A further eight sites had concentrations exceeding 2 µg/l.

Most chromium concentrations were less than 1 µg/l with the highest at 5.7 µg/l (sample 75). This is not exceptionally high compared to other UK groundwaters.

Most cobalt concentrations were below 0.1 µg/l, although Hartfell Spa contained an unusually high concentration (35 µg/l), reflecting its mineralised character. Only two other samples contained more than 1 µg/l. Sample 51, from the Carboniferous aquifer, contained 3.4 µg/l; and sample 74, from the Ordovician, contained 1.3 µg/l.

Yttrium concentrations were variable, with a median concentration of 0.06 µg/l. There were four groundwaters with more than 1 µg/l: the highest concentration is in the sample from Hartfell Spa (7.1 µg/l), from mineralised Lower Palaeozoic rocks, and the second highest in sample 42 (1.8 µg/l), from the Silurian aquifer.

Most zirconium concentrations were below the detection limit (0.02 µg/l), with only 5 waters containing detectable concentrations. The highest concentration was in sample 31 (0.8 µg/l), from the Carboniferous aquifer.

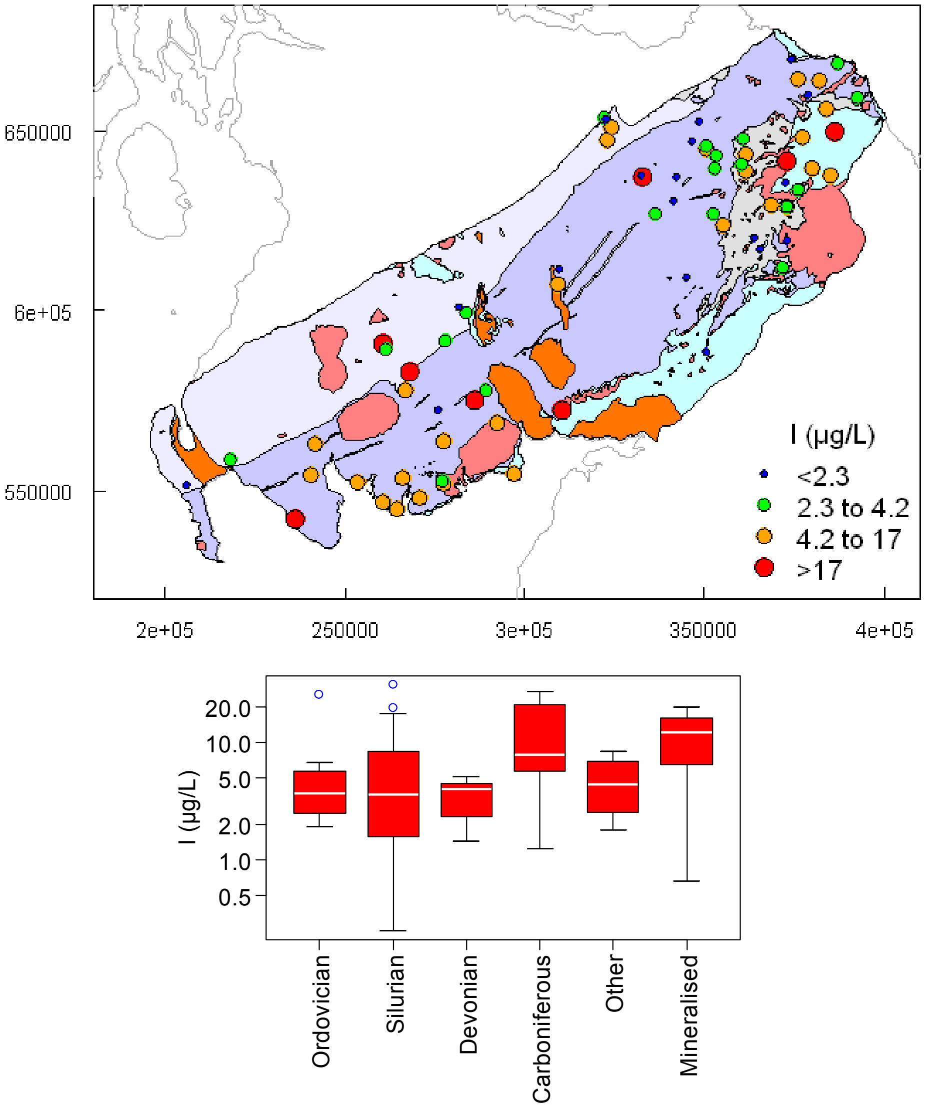
Only three groundwaters had detectable (above 0.01 µg/l) niobium concentrations. The maximum concentration was 0.03 µg/l.

There was only one groundwater (sample 53, from the Carboniferous) with a detectable (above 0.05 µg/l) silver concentration (0.09 µg/l).

Only seven waters had detectable (above 0.1 µg/l) mercury (Hg) concentrations, and the maximum concentration was 1 µg/l in sample 51, from the Carboniferous. However, Hg is strongly sorbed by most surfaces, including the sample bottles, and can also be lost by volatilisation during storage. Therefore, the reported concentrations are if anything minimum values. Special sampling methodology is required for reliable Hg estimation.

4.5.6 Iodine

Median iodide concentrations are about 3 µg/l for groundwaters from the Silurian, Ordovician and Devonian strata and somewhat greater for groundwaters from the Carboniferous strata and igneous rocks. These concentrations are typical of UK groundwaters and reflect contributions from rainfall, but may include contributions from mineralised strata and the decomposition of iodine-rich organic matter. A map and boxplot are shown in Figure 41.



The 'Other' category refers to igneous aquifers. The number of samples in each category is given in Table 2. For key to geology see Figure 5.

Figure 41 Boxplot and map showing the distribution of iodine concentrations in groundwater in aquifers across southern Scotland.

4.6 CUMULATIVE PROBABILITY PLOTS

Cumulative frequency plots provide an alternative way of looking at the distribution of element concentrations. They are complementary to the boxplots given above. We use them to provide a way of looking at a group of related elements in a single plot. The x-axis is the $\log_{10}$ transformed concentration (in units of mg/l) while the y-axis gives the probability of a value exceeding a given concentration, plotted on a normal probability scale. The log transform was chosen since many elements, especially the trace elements, show a near log normal distribution. The cumulative frequency (in percent) is 100 times the probability.

Although cumulative frequency plots could be usefully sub-divided by geology in the same way that the boxplots were, the limited number of samples in several of the geological sub-groups means that the steps in the plotted distributions would be too coarse and any benefits would be likely outweighed by the increased crowding of the resulting plots. We have therefore assumed that all 78 samples from the study area belong to a single population.

The plots make it easy to see the variation in the median concentrations between different elements (the points at which the probability is 0.5). The slopes of the lines give a measure of the variation (or standard deviation) of the subset of data and the straightness of the lines gives an indication of the extent to which the distribution follows a log-normal distribution. A distinct change in slope may indicate that the overall distribution is made up of two or more sub-populations with differing statistical properties. A tailing at the high concentration end is common and may indicate a population of contaminated or mineralised sites. However, since there is no law of nature that dictates that a particular distribution should exist, it is not possible to infer the origin or genesis of particular sets of samples purely on the basis of their position within a population. That would require more information including a model for what controls the concentration of a particular element within the sampled area. Similar reasoning applies to any attempt to distinguish ‘natural’ and ‘contaminated’ samples purely on the position within the overall distribution.

The cumulative probability plots were calculated on an element by element basis with the groups of elements determined by a common theme. Missing data were omitted. The NADA approach was chosen for calculating the probabilities, choosing the appropriate method for dealing with censored data according to the criteria outlined in Section 4.1.1. In most cases, the Kaplan-Meier method was used.

Three cumulative frequency probability plots are shown below: major elements (Figure 42); minor elements (Figure 43); and trace elements (Figure 44).

4.6.1 Major elements

The plot clearly shows the relative abundance of the major ions (in terms of mg/l) with HCO_3 being the most abundant and K and NO_3-N the least abundant. Concentrations are generally in the range 1 – 1000 mg/l. The slopes of the curves are broadly similar with the exception of NO_3-N which has a large tail at low concentrations (<3 mg/l reflecting areas with little agriculture and also changes in geochemical conditions (e.g. reducing conditions leading to nitrate reduction and exceptionally low concentrations).

The coarse steps at high concentrations reflect the small number of samples controlling the shapes of the curves at these concentrations. There is an indication of a change in slope of some of the curves at high concentrations, e.g. for Ca, Na, Cl and SO_4, reflecting the elevated concentrations in some of the Carboniferous samples, and also the mineralised springs.

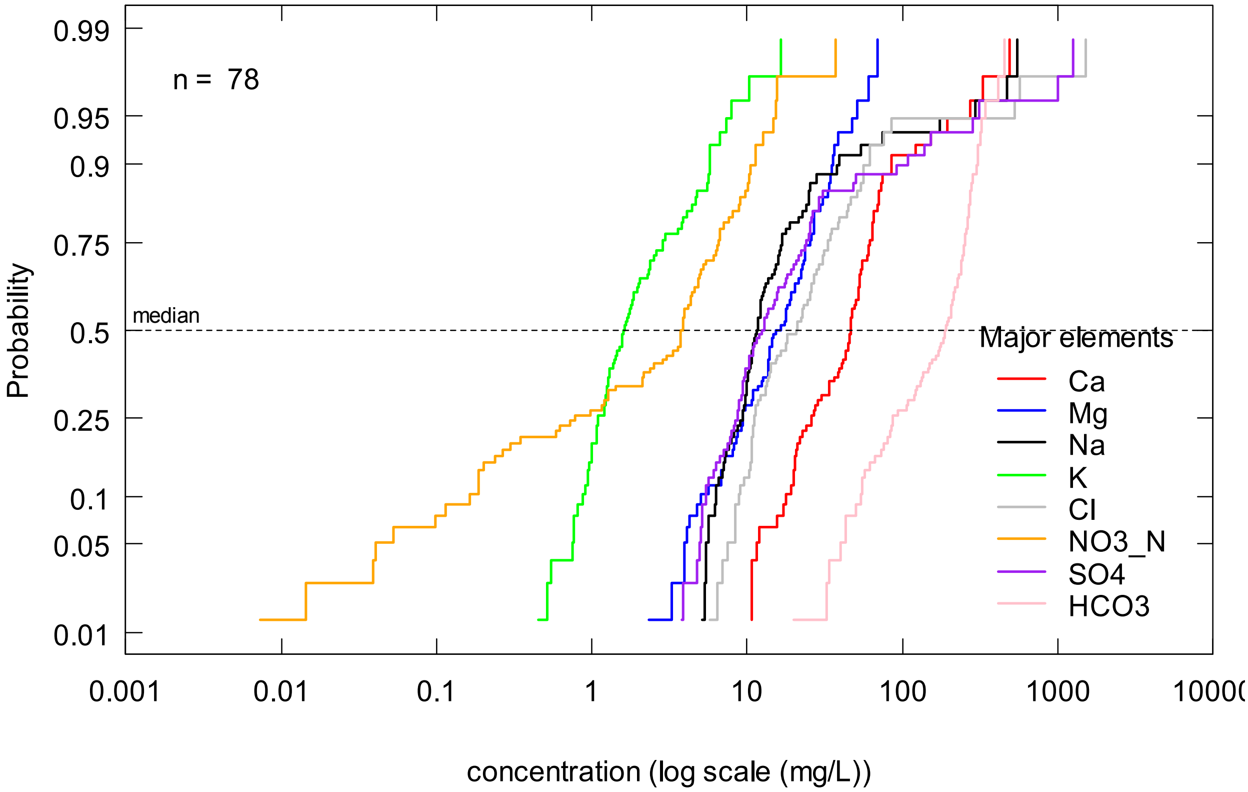


Figure 42 Cumulative probability plots for eight major elements.

4.6.2 Minor elements

The minor elements selected, mostly those with a neutral or negative charge, cover a wide range of concentrations, largely from 1 µg/l to 1 mg/l. Most of the curves are parallel to each other though NH_4-N has a much shallower slope indicating a broader distribution. This is possibly for somewhat similar reasons to those put forward for NO_3-N above. The tails at high concentrations, especially for Br and F, reflect the small number of mineralised areas included within the study. Iodide and nitrite do not show such a tail.

4.6.3 Trace elements

The cumulative probability curves reflect the range of concentrations observed, mostly below 0.01 mg/l (10 µg/l), and the detection limit of the analytical method used. The more abundant trace elements with no censored data, e.g. Zn and Cu, show relatively smooth curves, whereas it is more difficult to get information from the heavily censored elements such as Sc and Mo. The most censored elements in this data set are Ni and As for which more than half the samples (58% and 56%, respectively) had concentrations below their detection limits. The ROS method (Section 4.1.1) was therefore used for these. This method provides estimates of the probabilities for low concentrations, hence the linear stepped curves seen for As and Ni at low concentrations.

With some elements, such as U, there is evidence of a fairly straight curve indicating a single log-normally distributed population, whereas other elements, including Cu and Zn, showed gently curving plots indicative of somewhat positively skewed log-normal distributions.

The plots show how low the median concentrations of some biologically-important elements, such as Co, are in these waters.

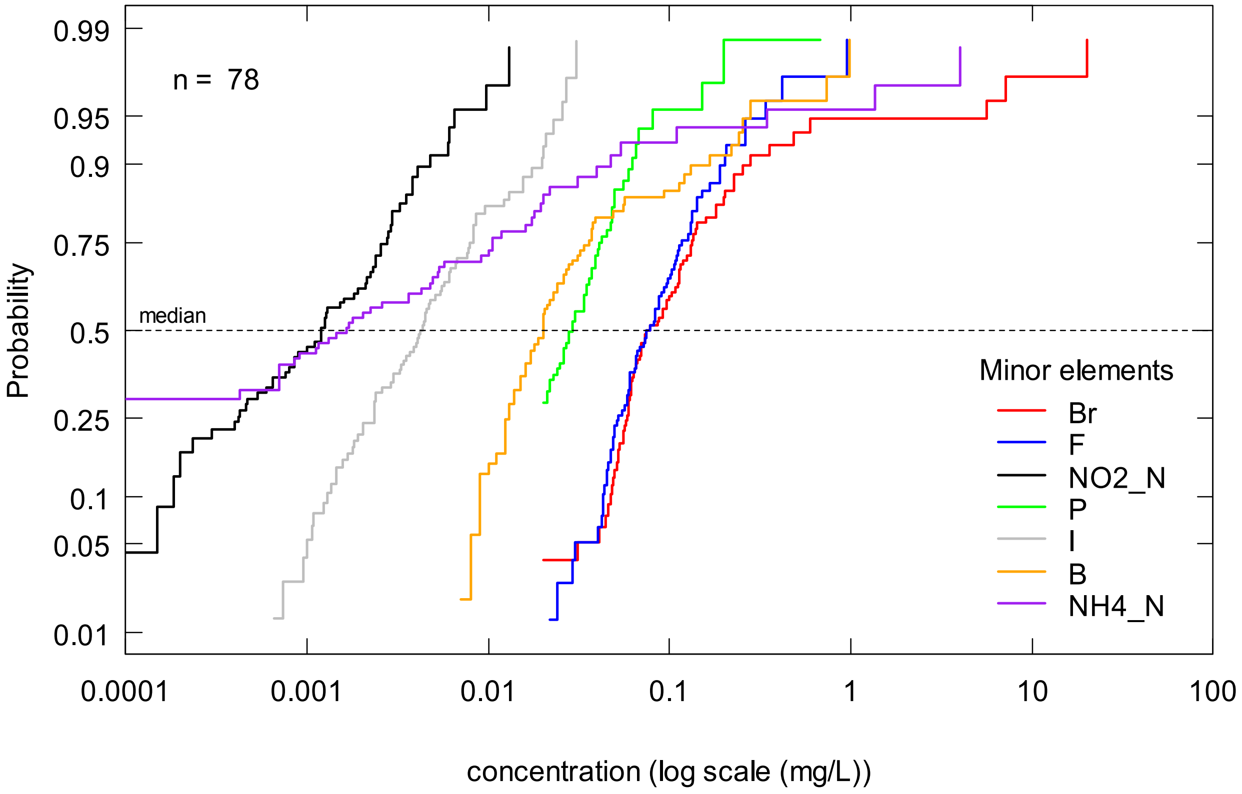


Figure 43 Cumulative probability plots for selected minor elements.

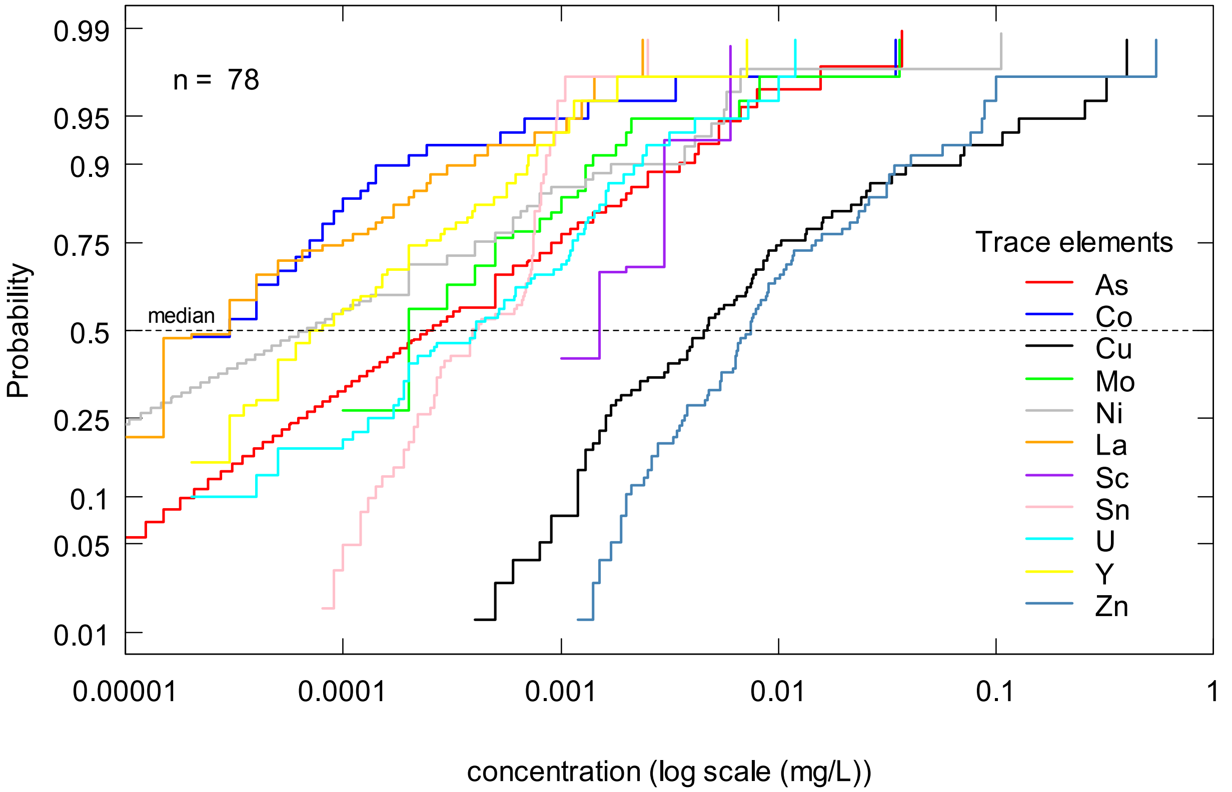


Figure 44 Cumulative probability plots for selected trace elements.

4.7 ENVIRONMENTAL TRACERS

4.7.1 Stable Isotopes

An isotope co-plot (Figure 45) shows that the samples fall on or close to the 'world meteoric line' (WML), defined by the empirically-determined relationship of $\delta^2H = 8\ \delta^{18}O + 10$, which has been found to hold good for most rainfall and groundwaters worldwide, particularly in temperate latitudes. This shows that, as would be expected in southern Scotland, none of the samples suffered evaporation at any point during the recharge–discharge process.

However, isotope values tend to change with geographical location (Figure 46), with less negative values in the southwest of the study area, and more negative values in the northeast (only $\delta^{18}O$ values are shown, but δ^2H shows a similar trend). There are two reasons for this: firstly a rainout effect as the predominantly southwesterly airflow passes over the land, and secondly the existence of relatively high elevations in the area. Most of the samples in the west of the study area were collected from the coastal area where elevations are low, though a few more negative compositions are seen (e.g. a value of –7.9 ‰ in sample 68, from the Silurian aquifer inland in the west). This indicates recharge from higher altitude. However, in the inland area northeast of Moffat, most samples have a depleted composition. If these northeastern samples are plotted relative to a typical altitude-related isotopic depletion of around 0.35 ‰ $\delta^{18}O$ per 100 m rise in altitude, it can be seen (Figure 47) that virtually all the samples are negative of the gradient line, to varying extents. This indicates that the water is being derived from differing recharge altitudes, with only samples nearer the line being recharged locally to the sampling site. The maximum depletion relative to the line is approximately 1 ‰ in $\delta^{18}O$; this would correspond to a recharge altitude approximately 300 m higher than indicated by the line. Thus, for example, the value of -9.14‰ $\delta^{18}O$ in sample 8, situated at 285 m above sea level (asl), actually suggests an average recharge altitude of 550–600 m asl. This would be consistent with the existence of maximum elevations of over 700 m in the area.

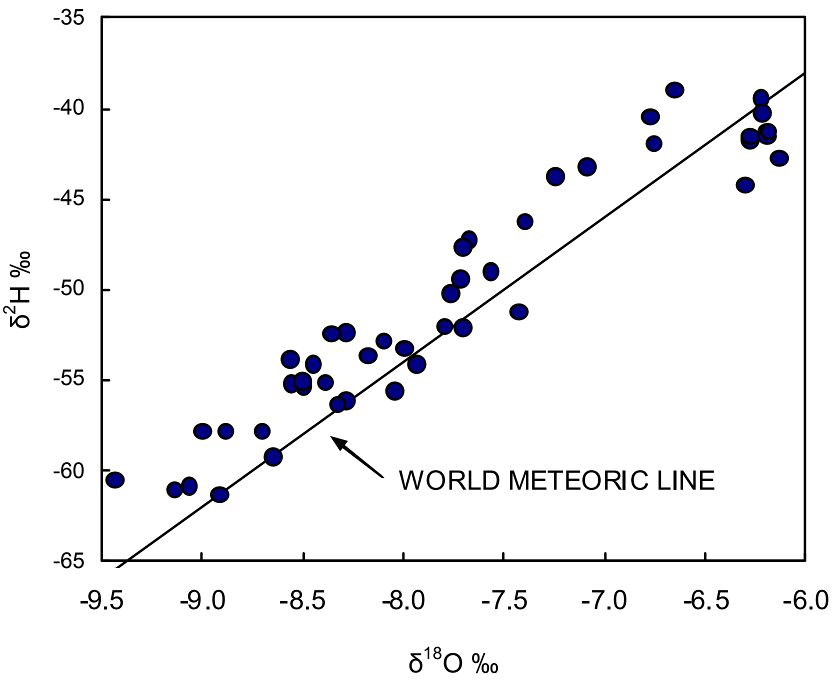


Figure 45 Isotopic co-plot showing the disposition of groundwater samples on or near the World Meteoric Line.

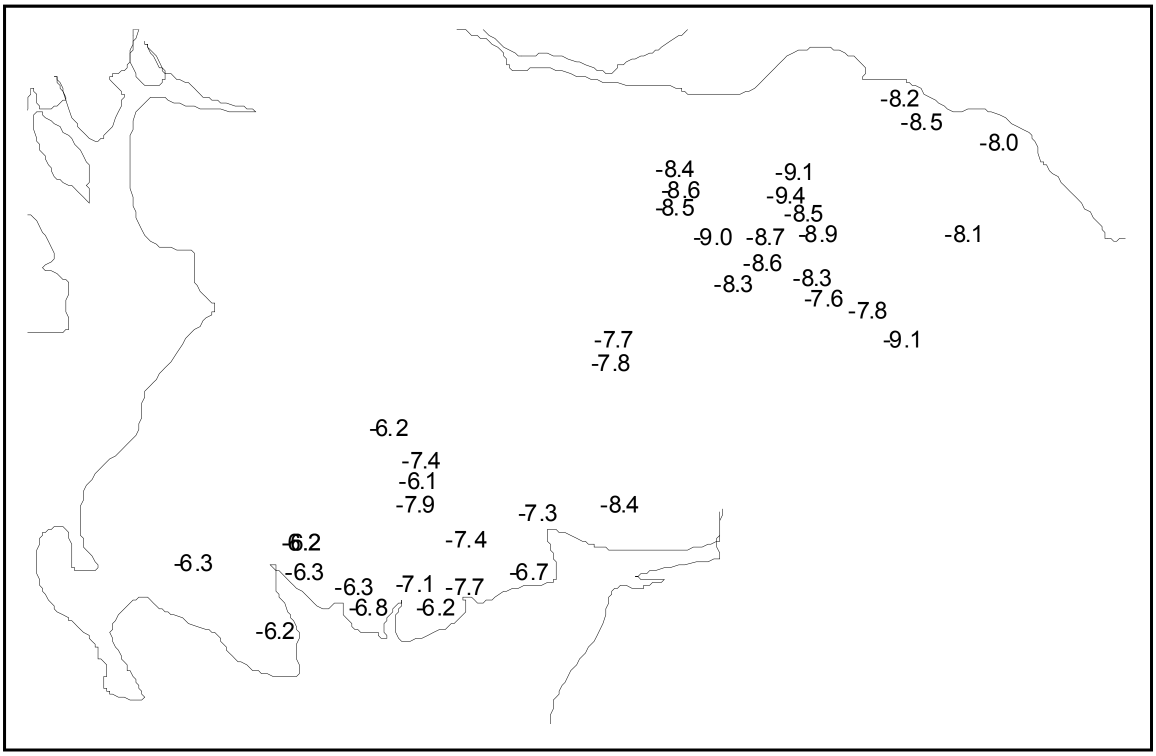


Figure 46 Map of groundwater samples in southern Scotland showing a general depletion in $\delta^{18}O$ values from southwest to northeast.

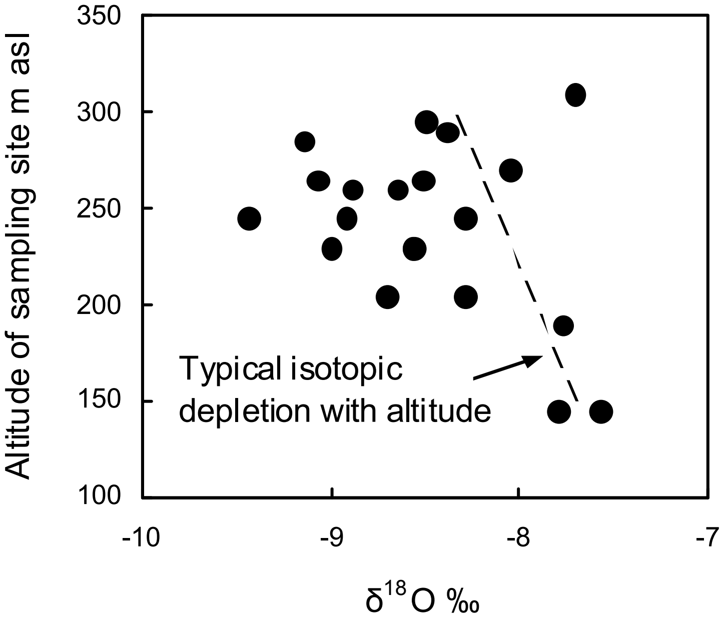


Figure 47 Plot of $\delta^{18}O$ versus altitude of sampling site. Some samples are more negative than would be expected for local recharge, suggesting that they are recharged up to ~300 m higher in elevation.

4.7.2 Residence-time indicators

CFCs (chlorofluorocarbons) and SF_6 (sulphur hexafluoride) were analysed for selected sites to provide an indication of groundwater residence time. According to the stable isotope evidence, many of the sites measured were at recharge elevations where the normal assumption of a mean annual recharge temperature (RT) may have been below the 10°C assumed for lowland Britain. However, the measured concentrations of CFCs and SF_6 were mostly low compared to present-day concentrations, so exact RT and excess air corrections therefore make rather little difference to residence-time calculations. For the higher concentrations seen in a few lowland samples, where RT is of greater significance, 10°C is probably the appropriate temperature to use. Therefore rather than using plots for two or more different RTs, Figure 48 shows a single plot of CFC-12 versus SF_6 for a temperature of 10°C and an excess-air correction of 0.5 for SF_6.

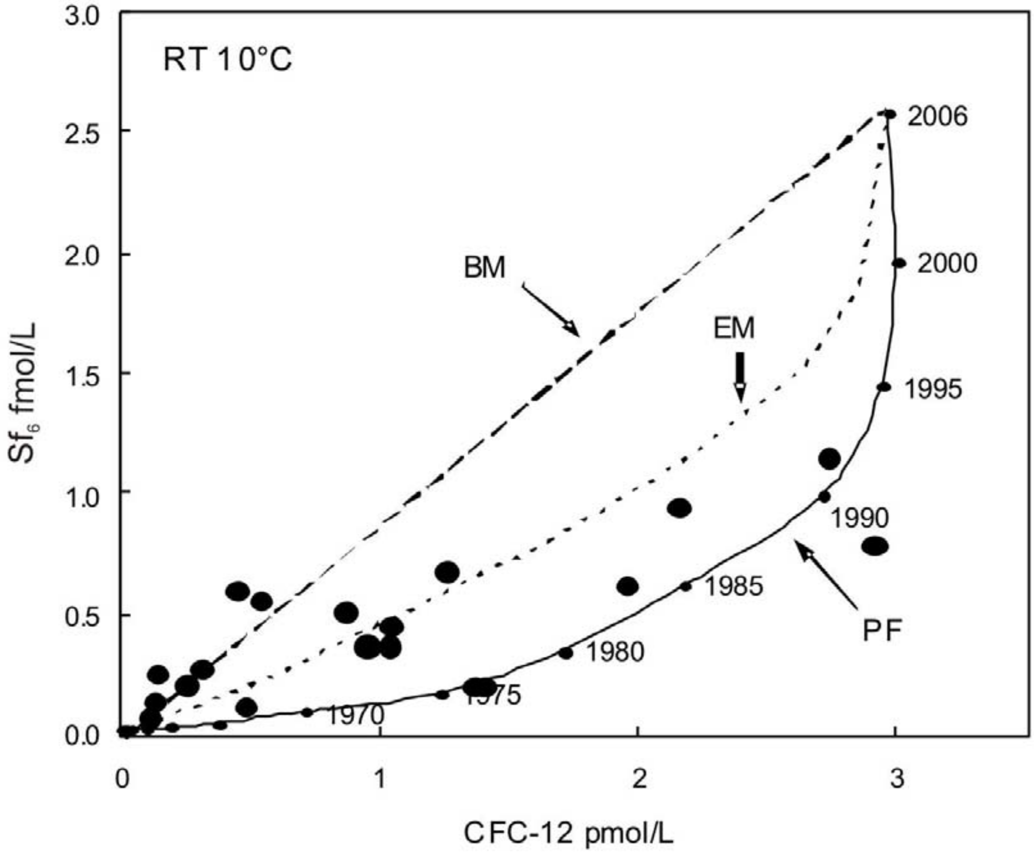


Figure 48 CFC-12 and SF_6 concentrations for groundwaters from southern Scotland plotted versus the 'piston flow' curve (PF), the binary mixing line (BM) between modern and old water, and the exponential mixing curve (EM).

The various curves (BM, EM and PF) represent theoretical compositions resulting from different modes of flow. Binary mixing (BM) is simple end-member mixing, while piston flow (PF) is simple flow without mixing. Exponential mixing (EM) refers to the probable statistical distribution where different flowpath lengths contribute to a particular borehole or spring. While each of these options is hydrogeologically feasible, in reality there may be some overlap between flow types. The plot indicates that most of the sampled groundwaters consist either of decades-old recharge, or mixtures (binary or exponential) where older water predominates. This would be consistent with flow from higher recharge altitudes as suggested by the stable isotope data. However, there are a few cases where more modern piston-flow or exponentially-mixed waters are present, though ages of at least 15 years are indicated.

5 Discussion

5.1 BASELINE GROUNDWATER CHEMISTRY

One of the reasons for undertaking this survey was to determine baseline groundwater chemistry conditions for the various groundwater units in Southern Scotland. Piper diagrams illustrate the distribution of these data for the four main aquifers (treating the Ordovician and Silurian as separate aquifers) (Figure 49). These show the groundwater chemistry of the different aquifer groups, and indicate outliers. Baseline chemistry can incorporate a range of chemical concentrations in groundwater in any one aquifer, influenced by natural processes including oxidation state and residence time dependency. As with previous baseline reports (e.g. Ó Dochartaigh et al. 2006) two approaches are taken. The main approach is statistical and allows for the natural variation in baseline chemistry that can occur, in which we examine the data between the 10th and 90th percentiles for each element or ion (see summary data in Tables 4, 5, 6 and 7). Using data between the 10th and 90th percentiles allows the influence of outliers to be minimised. We would expect new data to plot within this range 80% of the time. Data outwith this range can still occur naturally, but are less common and therefore may merit some further investigation. We have also applied a secondary approach to identify several individual samples from each aquifer, collected from groundwater sources where there is no evidence of contamination. These illustrate the observed range in chemical variation and can be used as reference groundwaters for management purposes.

The data presented in Section 4 indicate systematic variations in some solutes with geology. In the main aquifers, most noticeable is the saturation and supersaturation of calcite in groundwater from Devonian and Carboniferous aquifers and the lack of calcite in many of the samples from the Silurian and Ordovician aquifers. Another difference is the elevation of sulphate and potassium in groundwaters from the Carboniferous aquifer compared to other waters. Samples from igneous aquifers also have different groundwater chemistry to the main aquifers, but there are too few samples in this group to draw conclusions about the expected baseline chemistry that are statistically meaningful.

The baseline statistics are given for four aquifers: Lower Palaeozoic aquifers, divided into Silurian and Ordovician; Devonian sedimentary aquifers; and Carboniferous sedimentary aquifers. There is no significant systematic difference in groundwater chemistry between the Silurian and Ordovician aquifers (Tables 4 and 5). Concentrations of nitrate and phosphorus in the groundwater have generally been modified from pristine conditions due to anthropogenic (mainly agricultural) activity, and they are discussed in more detail in Section 5.3.

Table 4 Summary statistics for selected elements in groundwaters from Silurian aquifers in southern Scotland.

Element	Units	min	10%	25%	50%	75%	90%	max	n
pH	pH units	6.03	6.44	6.79	7.17	7.50	7.77	8.10	39
Eh	mV	277	306	345	394	427	474	534	35
DO	mg/l	0.0	0.4	2.6	3.9	5.2	8.3	11.2	37
SEC	µS/cm@25°C	87	165	249	402	540	599	689	39
Ca	mg/l	7.1	17.0	22.4	44.0	60.9	65.8	85.3	40
Mg	mg/l	1.7	4.2	7.9	13.7	18.3	25.7	33.8	40
Na	mg/l	4.3	5.6	7.4	10.8	15.4	19.2	25.6	40
K	mg/l	0.34	0.80	1.00	1.28	1.80	3.63	5.70	40
Cl	mg/l	5.2	8.9	10.7	16.0	31.5	45.0	75.6	40
SO_4	mg/l	3.0	4.9	6.2	10.0	13.5	20.5	28.8	40
HCO_3	mg/l	32.0	43.0	84.0	163	242	274	315	40
NO_3_N	mg/l	0.04	0.19	1.38	3.88	6.70	10.7	15.5	40
NO_2_N	mg/l	0.00007	*0.0002*	*0.0004*	0.0013	0.0025	0.0033	0.0061	39
NH_4_N	mg/l	<0.00005	*0.00012*	*0.00017*	0.0006	0.0046	0.0163	0.0475	39
DOC	mg/l	0.45	0.60	0.74	1.29	1.77	2.18	3.05	28
F	mg/l	0.019	0.039	0.045	0.058	0.082	0.102	0.204	40
Br	mg/l	0.000	0.047	0.058	0.071	0.116	0.146	0.254	40
I	mg/l	0.003	0.785	2.37	4.35	8.31	15.5	30.6	33
Si	mg/l	2.01	2.60	3.53	4.23	4.93	5.90	7.80	40
Fe	mg/l	*0.0001*	0.0006	0.0020	0.0033	0.0058	0.0124	0.0226	40
Mn	mg/l	0.0002	0.0003	0.0004	0.0014	0.0057	0.038	1.630	40
Sr	mg/l	0.019	0.057	0.095	0.165	0.250	0.279	0.443	40
Al	mg/l	0.001	0.002	0.004	0.005	0.010	0.014	0.033	40
P	mg/l	<0.02	<0.02	<0.02	0.0245	0.03525	0.0475	0.062	35

Concentrations in italics are below the limit of censored data and have been estimated using a ROS approach

Table 5 Summary statistics for selected elements in groundwaters from Ordovician aquifers in southern Scotland.

Element	Units	min	10%	25%	50%	75%	90%	max	n
pH	pH units	6.19	6.46	6.65	6.84	7.56	7.77	7.88	8
Eh	mV	101	189	258	314	388	417	461	8
DO	mg/l	0.1	0.5	1.7	5.1	5.9	7.1	8.0	7
SEC	µS/cm@25°C	178	241	275	298	338	414	585	8
Ca	mg/l	17.8	18.9	19.6	28.0	42.2	52.1	72.4	8
Mg	mg/l	5.1	7.3	9.1	12.3	13.7	15.1	17.7	8
Na	mg/l	7.3	7.7	8.2	9.7	12.5	14.9	15.7	8
K	mg/l	0.52	0.69	0.84	1.23	1.86	3.23	4.06	8
Cl	mg/l	7.5	8.1	10.3	11.1	15.6	23.9	25.8	8
SO_4	mg/l	7.1	8.0	9.0	9.9	16.4	23.7	29.2	8
HCO_3	mg/l	54.5	69.6	83.9	103	170	187	190	8
NO_3_N	mg/l	0.19	0.30	0.67	1.21	7.07	20.1	37.2	8
NO_2_N	mg/l	*0.0003*	*0.0004*	0.0006	0.0022	0.0045	0.0085	0.0130	8
NH_4_N	mg/l	*0.0001*	*0.00001*	0.00045	0.0024	0.0187	1.2230	3.9850	8
DOC	mg/l	0.96	1.02	1.26	2.21	3.40	3.70	3.74	6
F	mg/l	0.022	0.040	0.056	0.069	0.078	0.090	0.094	8
Br	mg/l	0.048	0.054	0.063	0.071	0.116	0.141	0.181	8
I	mg/l	1.91	1.98	2.46	3.33	5.67	14.3	25.5	7
Si	mg/l	2.44	3.34	3.85	4.07	5.36	6.43	7.21	8
Fe	mg/l	0.0017	0.0027	0.0034	0.0048	0.0954	0.584	1.18	8
Mn	mg/l	0.0007	0.0012	0.0016	0.0227	0.0767	0.234	0.577	8
Sr	mg/l	0.062	0.073	0.099	0.166	0.233	0.288	0.292	8
Al	mg/l	0.004	0.005	0.005	0.006	0.011	0.014	0.021	8
P	mg/l	<0.02	<0.02	<0.02	0.0025	0.0255	0.0264	0.027	4

Concentrations in italics are below the limit of censored data and have been estimated using a ROS approach

Table 6 Summary statistics for selected elements in groundwaters from Devonian aquifers in southern Scotland.

Element	Units	min	10%	25%	50%	75%	90%	max	n
pH	pH units	6.05	7.25	7.40	7.62	7.75	7.80	8.07	13
Eh	mV	314	324	335	346	413	434	446	7
DO	mg/l l	1.3	2.3	3.1	3.8	7.0	8.3	8.3	7
SEC	µS/cm@25°C	260	386	412	431	545	601	745	13
Ca	mg/l	27.6	41.5	45.7	46.5	48.8	61.9	85.4	13
Mg	mg/l	14.4	18.6	21.3	25.8	34.1	44.7	51.3	13
Na	mg/l	6.3	7.6	9.7	11.7	12.8	19.9	73.7	13
K	mg/l	1.19	1.28	1.57	2.00	2.39	3.68	4.44	13
Cl	mg/l	11.2	13.6	14.3	21.0	25.9	28.5	61.1	13
SO_4	mg/l	7.7	9.0	12.0	22.3	25.0	29.7	152.1	13
HCO_3	mg/l	93.9	179	207	216	272	302	453	13
NO_3_N	mg/l	0.163	1.39	2.35	3.88	7.65	9.74	11.3	13
NO_2_N	mg/l	0.0002	0.0003	0.0007	0.0011	0.0032	0.0049	0.0060	7
NH_4_N	mg/l	0.0002	*0.00003*	*0.00003*	*0.00008*	0.0030	0.0103	0.0180	7
DOC	mg/l	0.27	0.33	0.42	0.54	0.74	1.00	1.17	4
F	mg/l	0.074	0.082	0.098	0.108	0.131	0.141	0.151	13
Br	mg/l	0.025	0.045	0.049	0.064	0.075	0.098	0.598	13
I	mg/l	0.004	0.004	0.004	0.005	2.01	4.13	4.42	11
Si	mg/l	3.58	3.84	4.21	4.43	5.71	5.82	6.75	13
Fe	mg/l	*0.0003*	*0.0018*	0.0023	0.0028	0.0075	0.0105	0.0139	13
Mn	mg/l	0.0002	0.0003	0.0005	0.0010	0.0012	0.002	0.003	13
Sr	mg/l	0.030	0.052	0.064	0.129	0.179	0.382	2.127	13
Al	mg/l	0.001	0.002	0.004	0.005	0.006	0.008	0.017	13
P	mg/l	0.028	0.030	0.0385	0.045	0.062	0.068	0.152	11

Concentrations in italics are below the limit of censored data and have been estimated using a ROS approach

Table 7 Summary statistics for selected elements in groundwaters from Carboniferous aquifers in southern Scotland.

	Units	min	10%	25%	50%	75%	90%	max	n
pH	pH units	7.10	7.14	7.26	7.32	7.86	7.96	8.25	9
Eh	mV	155	161	171	282	289	399	472	5
DO	mg/l	0.2	0.8	1.6	2.7	3.5	3.8	4.1	4
SEC	µS/cm@25°C	469	551	616	1015	1800	2267	2600	10
Ca	mg/l	27.1	50.4	54.9	96.2	184	295	487	10
Mg	mg/l	11.8	18.1	24.5	32.8	38.1	61.1	68.8	10
Na	mg/l	6.2	11.6	18.9	32.7	50.5	203	467	10
K	mg/l	1.23	1.77	4.70	5.73	7.16	8.76	16.4	10
Cl	mg/l	8.4	25.3	33.3	45.9	53.6	130	532	10
SO_4	mg/l	14.9	15.7	48.7	100	303	1032	1243	10
HCO_3	mg/l	229	237	243	253	308	349	413	10
NO_3-N	mg/l	*0.007*	0.01	0.06	2.35	6.12	6.56	7.01	10
NO_2-N	mg/l	0.0002	0.0003	0.0005	0.0007	0.0011	0.0054	0.0097	6
NH_4-N	mg/l	0.00203	0.00342	0.00503	0.0580	0.2861	0.8530	1.3610	6
DOC	mg/l	1.00	1.03	1.09	1.17	1.35	1.46	1.53	3
F	mg/l	0.059	0.059	0.130	0.199	0.264	0.348	0.417	10
Br	mg/l	0.059	0.103	0.141	0.227	0.336	1.157	7.183	10
I	mg/l	0.006	0.007	0.014	0.027	7.84	15.0	23.1	7
Si	mg/l	3.63	4.52	5.40	5.64	6.92	8.49	13.7	10
Fe	mg/l	*0.0032*	*0.0003*	0.0014	0.0174	0.383	2.62	16.7	10
Mn	mg/l	0.0002	0.0019	0.0040	0.0196	0.0411	0.141	0.713	10
Sr	mg/l	0.119	0.155	0.855	1.25	7.29	13.62	14.5	10
Al	mg/l	0.001	0.002	0.003	0.004	0.006	0.295	2.860	10
P	mg/l	<0.02	<0.02	0.0108	0.027	0.0458	0.261	0.68	8

Concentrations in italics are below the limit of censored data and have been estimated using a ROS approach

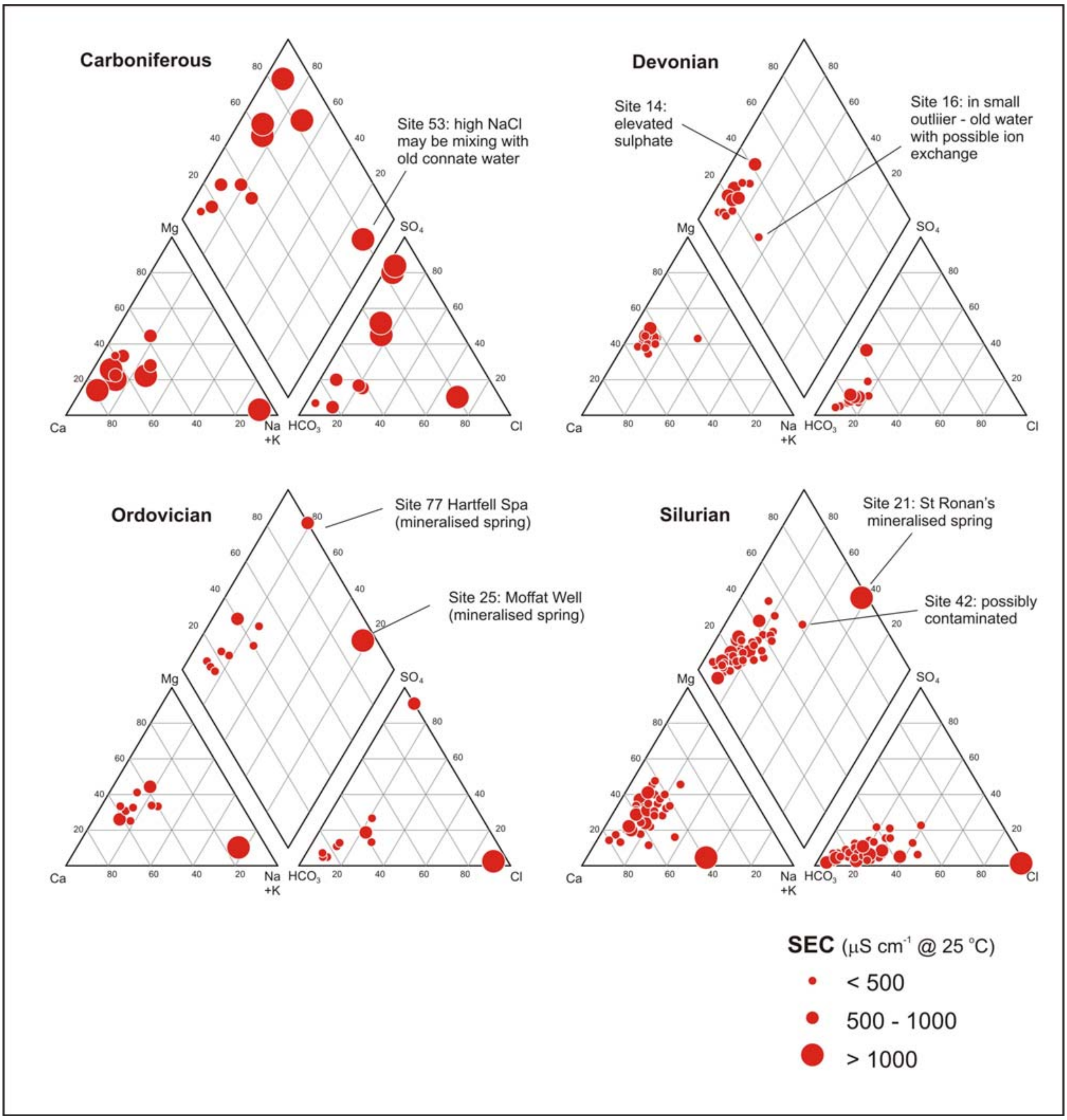


Figure 49 Piper diagram of major ion groundwater chemistry for southern Scotland.

As a secondary approach to identify baseline groundwater chemistry, ten groundwater samples from across the region have been selected as representative of the general observed groundwater chemistry. The chemistry of each sample broadly falls within the 10th to 90th percentile ranges for each aquifer as presented in Tables 4, 5, 6 and 7, and the groundwater sources from which the samples were collected are not subject to contamination. Older groundwaters and those where NO_3-N is below 10 mg/l were preferred. Since elevated nitrate concentrations are so widespread in groundwater across the region, to limit baseline sites to those with negligible nitrate or even nitrate below 4 mg/l NO_3-N (taken as the upper limit of naturally occurring nitrate in the region) would be too restrictive. At least two samples were chosen for each aquifer. Although no systematic differences in chemistry were found between the Ordovician and Silurian aquifers, samples from each were selected to represent their spatial distribution across the region: two for the Ordovician and four for the Silurian aquifer.

Two samples were selected as representative of the range of groundwaters in the Carboniferous aquifer, one of which particularly indicates more mineralised Carboniferous water. Two samples were also selected for the Devonian aquifer. The location of the samples related to the aquifer distribution across southern Scotland is shown in Figure 50.

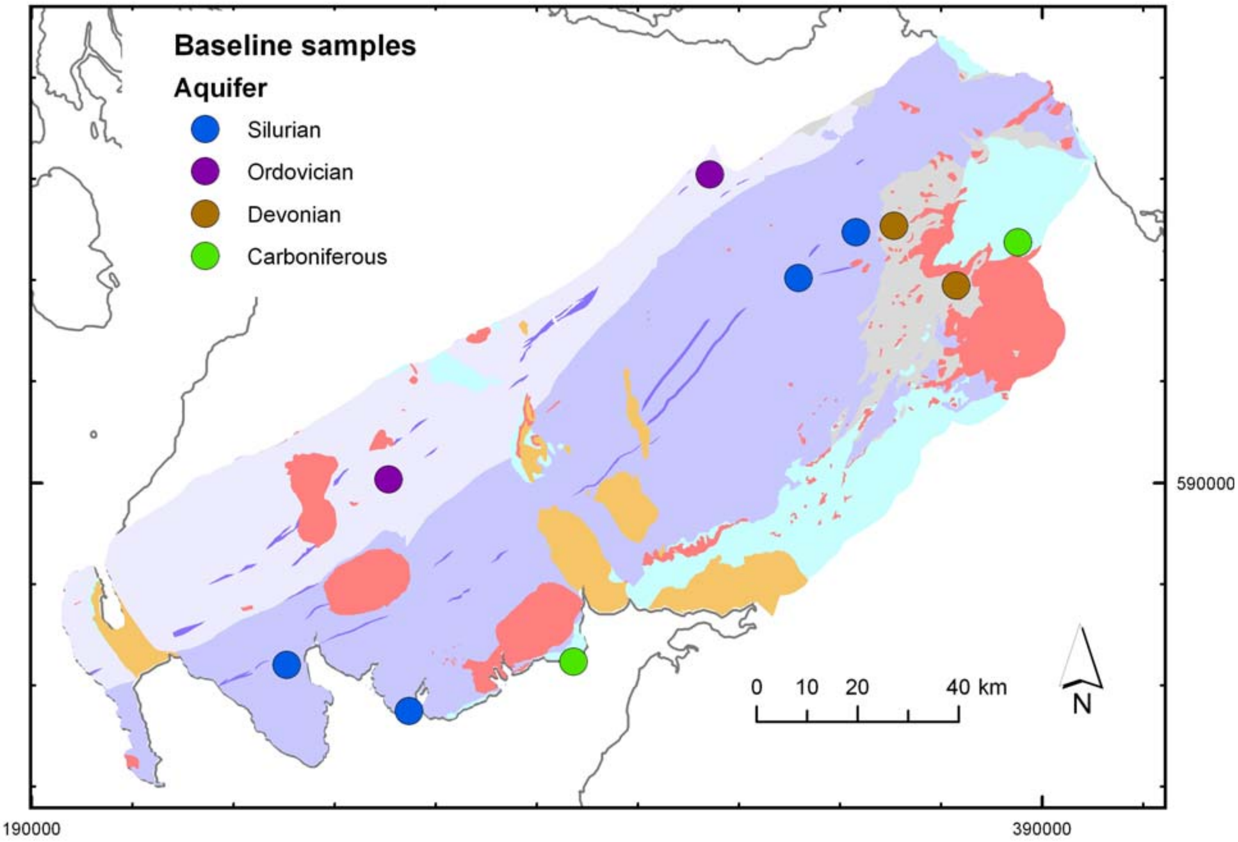


Figure 50 Location of the ten representative baseline samples across southern Scotland

5.2 EXCEEDANCES ABOVE DRINKING WATER STANDARDS

The chemical results of our survey were compared with (i) Scotland's statutory drinking water standards under The Water Supply (Water Quality) (Scotland) Regulations 2001 as regulated by the Drinking Water Quality Regulator (DWQR) for Scotland (Source = DWQR), and (ii) the 2004 WHO Guideline values for drinking water, 3rd Edition (Source = WHO).

Generally, the sampled groundwaters fall within current guidelines and regulations for drinking water. However, 26 DWQR exceedances were found covering six parameters (with numbers of exceedances in parentheses): Al (2), As (2), Mn (12), Na (3), Ni (1) and NO_3 (6). In addition, a further two samples failed the WHO guidance value for B (the WHO limit for B is more strict than the DWQR limit) and four samples failed the WHO guidance value for Ba (no limit is given by DWQR).

Not all the sampled waters are from drinking water supplies. While all exceedances should be followed up, perhaps the most significant (if confirmed) is the high As concentration recorded in sample 31 (37 µg/l (although the borehole from which this sample was taken is not currently used for drinking water). Although this sample contained detectable dissolved oxygen (2 mg/l), this was probably introduced at the surface: the water at depth is almost certainly reducing, which explains the high dissolved Fe concentration. The dissolved Fe would precipitate as an iron hydrous oxide on aeration at the surface and this would probably adsorb much of the As.

Also significant is manganese, which is the parameter which most frequently results in failure to meet drinking water standards. Some 15% of sites sampled had Mn concentrations in excess of the DWQR standard of 50 µg/l, of which at least four sites are used for drinking water supplies. Such elevated concentrations are common throughout Scotland (MacDonald et al. 2005) and are in part due to the variable pH and redox conditions found in Scottish groundwaters. Work is ongoing at BGS to examine in more detail controls on manganese mobilisation across Scotland.

The greatest exceedances in terms of the ratio of observed concentration to standard (or guideline) value were for Ba and Al. Not surprisingly the mineralised waters gave a disproportionately high proportion of the noted exceedances.

5.3 NITRATE AND PHOSPHORUS

Median concentrations of nitrate concentrations across all geological formations are less than 5 mg/l NO_3-N, with most concentrations being less than the drinking water limit of 11.3 mg/l NO_3-N (50 mg/l NO_3) (Figure 25). Concentrations are related to land use. Using the same methodology as MacDonald et al. (2005) to characterise sites into different land use classes, groundwater from agricultural land is shown to have higher nitrate concentrations than that from non-agricultural land (Figure 27). The highest median nitrate concentration was beneath improved pasture land used for rearing dairy, pigs and poultry, as found in other parts of Scotland (MacDonald et al. 2005).

Elevated nitrate concentrations (> 5 mg/l as NO_3-N) are found outwith the current designated NVZ areas (Figures 2 and 25). The most noticeable area in this respect is in Galloway, where high concentrations are associated with improved pasture, and in particular dairy farming. Residence time indicators were used to examine nitrate concentrations further. These indicate a tendency towards a build-up of nitrate according to the fraction of modern water present (Figure 51). While the correlation is not particularly strong, there is a trend between sources on semi-natural land (older groundwater) and some of the arable and improved pasture sites (younger/higher proportion of recent groundwater). This also indicates that some of the measured nitrate concentrations in groundwater may be underestimating nitrate in recharge, due to mixing and dilution with older groundwaters.

The cumulative probability plot for nitrate (Figure 42) shows a bimodal distribution. This can be interpreted as a natural sample set, affected by soil reactions and possibly by nitrate reduction, and a sample set affected by anthropogenic contamination. The split between these populations lies between 3 and 4 mg/l, which is consistent with maximum concentrations measured in semi-natural and woodland areas. Concentrations of nitrate in excess of 4 mg/l could therefore be considered as non-natural. This is slightly higher than the baseline estimated for pre-1950s groundwater in the Permian aquifer in Dumfries (2 mg/l as NO_3-N) (MacDonald et al. 2003).

Phosphorus in groundwater can be an important influence on surface water eutrophication by providing baseflow to streams and rivers. SEPA have set limits of 8 µg P/l for oligotrophic surface waters, 25 µg P/l for mesotrophic waters and 80 µg P/l for eutrophic surface waters, based on annual geometric mean concentrations. The distribution of phosphate concentrations showed an overall median concentration of 29 µg P/l (Figure 31). Maximum concentrations were close to or below 100 µg P/l for most of the formations. Median P concentrations for the various formations tended to fall in the range 30-70 µg P/l, which is in the mesotrophic range for surface waters.

P concentrations do not show any strong relationship with land use (Figure 32) and the highest median P concentration was found under woodland. This illustrates the complexity of P geochemistry and the important role that soil geochemistry plays in the mobilisation of P into groundwater.

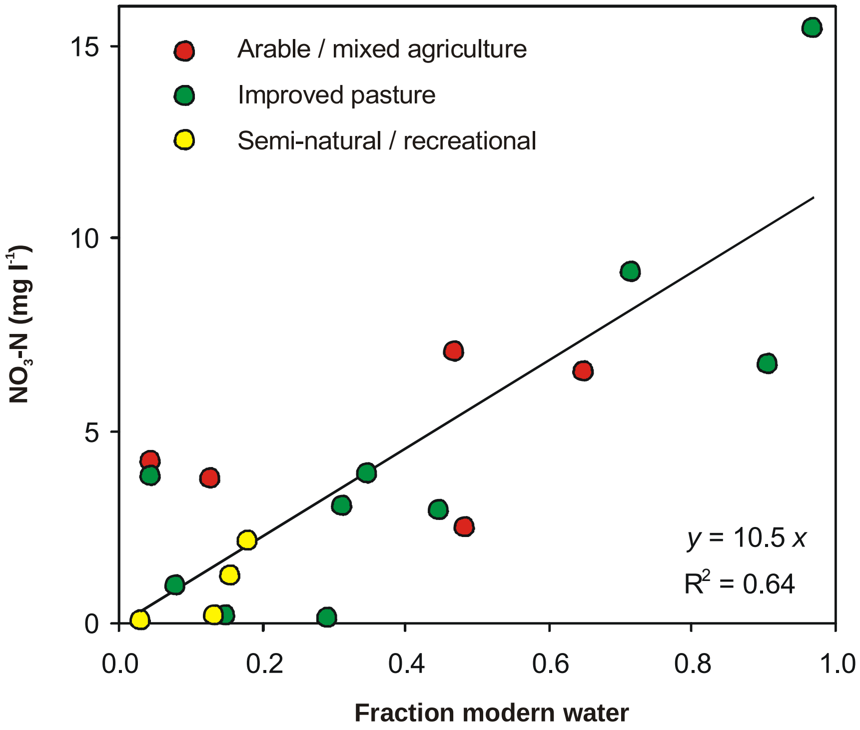


Figure 51 Nitrate concentrations versus fraction of modern water in groundwaters from southern Scotland.

5.4 THE MINERALISED SPRINGS

The mineralised springs from Lower Palaeozoic aquifers are a special case; they are excluded from the baseline discussions above and are described separately here.

The water quality of the three mineralised springs sampled, as well as the freshwater spring adjacent to St Ronan's Sulphur spring, are given in Table 8. The three mineralised springs are quite different in their chemical compositions. St Ronan's Sulphur Spring is the most mineralised with high concentrations of Na, Ca and Cl and a wide range of trace constituents, notably Ba, Br, Li, I, Rb and Mn. Surprisingly, its total sulphur content (i.e. sulphate + sulphide) was lower than the fresh water spring. There were signs of yellow sulphur deposits and a 'sulphurous' smell at the sampling site. The measured dissolved oxygen was easily detectable at 3 mg/l and the sample had an Eh of 265 mV (not strongly reducing) and so it is likely that some oxidation had taken place. This would precipitate the yellow solid sulphur observed since it is well known that sulphur is a frequently observed intermediate in the oxidation of sulphide to sulphate. The nearby freshwater spring showed no signs of sulphur precipitation.

Hartfell Spa is known as a chalybeate ('iron-rich') spring. It is strongly acidic with high concentrations of Fe, Al, Si, Mn, SO_4 and a wide variety of trace metals including Ni, Co, Cu, Y, Tl, Be, Sc, Zn, Sn and REE.

Groundwater from the nearby Moffat Well is slightly alkaline, probably reducing, and rich in Na-Cl. It contains high concentrations of Ba, Ge, Li, Br and B. It also contains slightly elevated concentrations of some REE, though many remained below the detection limit. It was one of only two groundwaters to show detectable Au and had the highest Au concentration observed in this study (0.41 µg/l). The aquifer source of the groundwater is uncertain, but it may be associated with the Moffat Shale Group. This group is found as small outliers throughout the area, associated with faults.

Table 8 Selected chemistry of the three mineralised springs and one freshwater spring sampled in southern Scotland

Site-name	**Units**	**St Ronan's freshwater spring (Sample 20)**	**St Ronan's Sulphur spring (Sample 21)**	**Hartfell Spa (Sample 77)**	**Moffat Well (Sample 25)**
Temp	°C	12.4	10.5		10.2
SEC	µS/cm	190	4650	522	1350
pH		7.72	7.1	3.68	7.71
Eh	mV	371	265		23
DO	mg/l	3.5	3.0		2.4
$\delta^{18}O$	‰	-9.00	-8.7		-7.77
$\delta^{2}H$	‰	-57.8	-57.8		-50.2
Br	mg/l	0.04	20.3	<0.02	5.7
Ca	mg/l	19.9	328	10.6	45.1
Cl	mg/l	10.4	1500	5.7	563
DOC	mg/l	0.8	0.8	1.3	3.9
F	mg/l	0.1	0.1	0.1	1.0
Fe	mg/l	0.02	0.9	7.6	0.02
HCO_3	mg/l	55.5	56.7	<20	83.0
K	mg/l	0.8	10.3	0.8	3.0
Mg	mg/l	4.8	23.1	7.1	19.1
Na	mg/l	7.6	543	5.5	295
NO_3-N	mg/l	1.3	0.3	0.1	0.1
Si	mg/l	4.7	4.3	20.6	4.8
S as SO_4	mg/l	15.5	5.4	138	17.8
Sr	mg/l	0.1	23.4	0.04	5.2
Al	µg/l	14.0	11.0	10000	15.0
As	µg/l	<0.5	8.0	<0.5	1.9
B	µg/l	8.0	94.0	6.0	253.0
Ba	µg/l	5.0	24400	42	15200
Be	µg/l	<0.05	<0.5	0.9	<0.05
Cd	µg/l	<0.05	<0.5	0.6	<0.05
Ce	µg/l	0.1	<0.1	6.2	0.1
Co	µg/l	<0.02	<0.2	35	0.03
Cr	µg/l	<0.5	<5	2.5	<0.5
Cs	µg/l	0.0	<0.1	0.1	0.1
Cu	µg/l	0.9	7.7	401	3.8
Dy	µg/l	0.01	<0.1	1.6	0.03
Er	µg/l	<0.01	<0.1	0.7	0.01
Eu	µg/l	<0.01	<0.1	0.5	<0.01
Ga	µg/l	<0.05	<0.5	<0.05	<0.05
Gd	µg/l	0.01	0.2	2.0	0.2
Ge	µg/l	<0.05	<0.5	<0.05	4.1
Hf	µg/l	<0.02	<0.2	<0.02	<0.02
Hg	µg/l	<0.1	<1	<0.1	0.1
Ho	µg/l	<0.01	<0.1	0.3	<0.01
In	µg/l	<0.01	<0.1	0.01	<0.01
I	µg/l	0.7	20	0.7	12.1
Ir	µg/l	<0.05	<0.5	<0.05	<0.05
La	µg/l	0.1	0.1	2.4	0.2
Li	µg/l	2.1	535	8.4	347
Lu	µg/l	<0.01	<0.1	0.1	0.01
Mn	µg/l	2.3	729	694	55.4

Site-name	Units	St Ronan's freshwater spring (Sample 20)	St Ronan's Sulphur spring (Sample 21)	Hartfell Spa (Sample 77)	Moffat Well (Sample 25)
Nd	µg/l	0.1	<0.1	5.2	0.1
Ni	µg/l	<0.2	<2	106	<0.2
P	µg/l	35	<200	<20	<200
Pb	µg/l	<0.1	<1	2.7	<0.1
Pr	µg/l	0.0	<0.1	1.0	0.02
Rb	µg/l	0.8	12.1	2.4	2.9
Sb	µg/l	0.1	<0.5	<0.05	<0.05
Sc	µg/l	2.0	<10	6.0	<10
Sm	µg/l	<0.02	<0.2	1.7	0.1
Sn	µg/l	0.4	0.8	1.0	0.9
Tb	µg/l	<0.01	<0.1	0.3	<0.01
Tl	µg/l	<0.01	<0.1	0.7	<0.01
Tm	µg/l	<0.01	<0.1	0.1	<0.01
U	µg/l	0.2	<0.2	3.2	<0.02
V	µg/l	<0.2	<2	<0.2	0.9
W	µg/l	<0.02	<0.2	<0.02	0.2
Y	µg/l	0.04	0.2	7.1	0.2
Yb	µg/l	<0.01	<0.1	0.6	0.2
Zn	µg/l	1.7	9.0	87	4.8

5.5 GROUNDWATER FLOW IN SOUTHERN SCOTLAND

The hydrochemistry data and information on groundwater residence times help give an insight into groundwater flow in the different aquifers in southern Scotland. The best interpretation of the groundwater flow system within all of these aquifers is that it is largely through fractures, and well mixed in the top 50 metres or so. This interpretation is supported by the lack of correlation of nitrate with source depth across the region, and by the relative proportions of CFC and SF_6 concentrations, which indicate mixing rather than piston flow models.

There is no evidence of paleaowater in the area, and (where CFC and SF_6 have been measured) all samples recorded some proportion of water less than 50 years old. However, groundwater, even in the more fractured less permeable Lower Palaeozoic aquifers, can be resident for several decades.

Groundwater samples in the upland areas of southern Scotland often contain a large element of water that fell as rain on higher ground (as implied by depleted stable isotope data). This suggests connected groundwater systems, or possible in some instances reinfiltration of upland runoff into the groundwater systems.

6 Conclusions

The groundwater chemistry of bedrock aquifers in southern Scotland has been investigated using new chemistry analyses, generated during the Baseline Scotland project, combined with existing analyses from earlier projects. The chemistry of groundwater from four major and one minor aquifer group has been examined: the major groups are Lower Palaeozoic sedimentary and metasedimentary rocks (divided into Ordovician and Silurian), Devonian sedimentary rocks, and Carboniferous sedimentary rocks; the minor group comprises the small outcrops of igneous rocks that occur across the region.

A total of 47 new samples were collected for analysis between September 2005 and July 2006. These new samples were augmented with a further 31 samples collected during separate BGS projects since 2002. The sites were chosen to be representative of groundwater in the area, and sources that were very poorly constructed were avoided.

An estimate of the baseline groundwater chemistry conditions has been given for the four main aquifer units: Silurian and Ordovician aged sedimentary and metasedimentary rocks, and Devonian and Carboniferous sedimentary rocks. The baseline is given using a statistical summary of the chemical data, representing data between the 10th and 90th percentiles, with the exception of NO_3-N and P, where the influence of anthropogenic activity is likely to have distorted baseline conditions throughout much of the aquifer.

This statistical approach to estimating baseline was complemented by selecting ten analyses of groundwater samples collected from high quality groundwater sources, which are unlikely to have been impacted by any agricultural contamination, and which represent the general the groundwater conditions in the Silurian, Ordovician, Devonian and Carboniferous aquifers.

1. In all the aquifers sampled, groundwater flow is largely through fractures and is well mixed in the top 50 metres or so. There is no evidence of palaeowater in the area, and all samples recorded some proportion of water less than 50 years old. However, groundwater can be resident for several decades, even in the more fractured, less permeable Lower Palaeozoic aquifers.
2. Most of the groundwater pH values are in the near-neutral range (6.5–8.5). Groundwaters from Ordovician and Silurian aquifers tend to have a slightly lower pH than those from Devonian and Carboniferous aquifers. Groundwaters from igneous and mineralised Lower Palaeozoic aquifers are more acidic, with occasional pH values below 6.5.
3. Similar patterns to pH are observed in bicarbonate alkalinity, with HCO_3 in the range 100–250 mg/l for Ordovician and Silurian groundwaters, 200–320 mg/l for Devonian and Carboniferous groundwaters, and <100 mg/l for igneous and mineralised Lower Palaeozoic groundwaters. Cl and SO_4 concentrations are generally low, reflecting inputs from rainfall, with the exception of Carboniferous groundwaters which tend to have highest concentrations of Cl and SO_4, possibly reflecting the influence of connate water and sulphide mineralisation within interbedded mudstone.
4. Concentrations of the major cations reflect a combination of rainfall input, mineral weathering, and anthropogenic inputs derived from the use of fertilisers and liming, or from other sources of pollution. Most notable is an enrichment of K (5–10 mg/l) in groundwaters from Carboniferous sedimentary rocks, probably resulting from feldspar weathering. Ca concentrations broadly reflect the distribution of calcite in aquifer rocks. Groundwater from Ordovician, Silurian and mineralised strata and igneous aquifers are undersaturated with respect to calcite, as would be expected from their

non-carbonate mineralogy. Groundwater from the Devonian and Carboniferous strata are generally saturated or supersaturated with respect to calcite, indicating the presence of calcite either as a major (Carboniferous limestone) or minor (calcite cement in Devonian sandstones) component. There is a good positive correlation between Mg and Ca concentrations, especially for low Ca concentrations (<80 mg/l).

5. Most of the groundwaters in the study area are oxidising, with dissolved oxygen concentrations in the range 1–7 mg/l and a redox potential (Eh) greater than 300 mV. However, the mineralised springs are reducing, with sulphate reduction indicated at St Ronan's Well. Groundwaters from Carboniferous strata in general tend to be slightly less oxidising than those from other aquifers. Apart from these incidences, however, the groundwater redox status does not appear to vary strongly with geology.
6. In each of the aquifer groups the median concentration of nitrate in groundwater is less than 5 mg/l NO_3-N; in each group except the Ordovician aquifer, at least 90% of samples show nitrate concentrations that are less than the drinking water limit of 11.3 mg/l NO_3-N (50 mg/l NO_3). Concentrations are related to land use, with groundwaters beneath agricultural land showing higher concentrations than beneath non-agricultural land. The land use classification showing the highest median NO_3 concentration was land used for rearing 'dairy, pigs and poultry', as found in other parts of Scotland (MacDonald et al. 2005).
7. Elevated nitrate concentrations (> 5 mg/l NO_3-N) are found outwith the current designated Nitrate Vulnerable Zones (NVZs). The most noticeable are in the west of the study area in Galloway, where high concentrations are associated with improved pasture, and in particular dairy farming.
8. Phosphorus in groundwater can be an important influence on surface water eutrophication if present in baseflow to streams and rivers. Median P concentrations for the aquifer units in southern Scotland tend to fall in the range 30-70 µg/l-P. Phosphate concentrations do not show any strong relationship with land use, illustrating the complexity of P geochemistry, and the important role that soil geochemistry plays in the mobilisation of P into groundwater.
9. Three mineralised springs were sampled in southern Scotland: Moffat Well, St Ronan's Sulphur Spring and Hartfell Spa. These show variable chemical compositions. St Ronan's Sulphur Spring is the most mineralised, with high concentrations of Na, Ca and Cl, and a wide range of trace constituents, notably Ba, Br, Li, I, Rb and Mn. Hartfell Spa is known as a chalybeate ('iron-rich') spring, and is strongly acidic with high concentrations of Fe, Al, Si, Mn and SO_4, and a wide variety of trace metals, including Ni, Co, Cu, Y, Tl, Be, Sc, Zn, Sn and many of the rare earth elements. The nearby Moffat Well is slightly alkaline, probably reducing, and rich in Na and Cl. It contains high concentrations of Ba, Ge, Li, Br and B. It was one of only two groundwaters in the study to show detectable Au, and had the highest observed Au concentration (0.41 µg/l).

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Appendix 1 Description of sampling sites

ID	Field ID	Lab Sample ID	Project	Source type	Depth (m)	Land use
1	B004	S05-00247	SGMN	Spring	0 m	pasture
2	B007	S05-00248	SGMN	Spring	0 m	woodland
3	BR001	S05-00590	Baseline Borders	Borehole	> 100 m	arable
4	BR002	S05-00591	Baseline Borders	Borehole	30 - 100 m	pasture
5	BR003	S05-00592	Baseline Borders	Borehole	30 - 100 m	arable
6	**BR004**	**S05-00593**	**Baseline Borders**	**Borehole**	**30 - 100 m**	**mixed agricultural**
7	**BR005**	**S05-00594**	**Baseline Borders**	**Borehole**	**30 - 100 m**	**pasture**
8	BR006	S05-00595	Baseline Borders	Borehole	30 - 100 m	pasture
9	BR007	S05-00596	Baseline Borders	Spring	0 m	semi natural
10	BR008	S05-00597	Baseline Borders	Spring	0 m	pasture
11	BR009	S05-00598	Baseline Borders	Spring	0 m	semi natural
12	BR010	S05-00599	Baseline Borders	Borehole	30 - 100 m	semi natural
13	BR011	S05-00600	Baseline Borders	Borehole	30 - 100 m	pasture
14	BR012	S05-00601	Baseline Borders	Borehole	30 - 100 m	recreational
15	BR013	S05-00602	Baseline Borders	Borehole	30 - 100 m	woodland
16	BR014	S05-00603	Baseline Borders	Borehole	30 - 100 m	pasture
17	BR015	S05-00604	Baseline Borders	Borehole	30 - 100 m	pasture
18	**BR016**	**S05-00605**	**Baseline Borders**	**Borehole**	**30 - 100 m**	**semi natural**
19	BR017	S05-00606	Baseline Borders	Borehole	30 - 100 m	pasture
20	BR018	S05-00607	Baseline Borders	Spring	0 m	semi natural
21	BR019	S05-00608	Baseline Borders	Spring (min)	0 m	semi natural
22	**BR020**	**S05-00609**	**Baseline Borders**	**Borehole**	**30 - 100 m**	**semi natural**
23	BR021	S05-00610	Baseline Borders	Borehole	30 - 100 m	semi natural
24	BR023	S05-00612	Baseline Borders	Spring	0 m	pasture
25	BR024	S05-00613	Baseline Borders	Spring (min)	0 m	semi natural
26	BR026	S05-00615	Baseline Borders	Borehole	unknown	pasture DPP
27	BR027	S05-00616	Baseline Borders	Borehole	unknown	pasture DPP
28	K001	S05-00264	SGMN	Spring	0 m	semi natural
29	K002	S05-00265	SGMN	Borehole	30 - 100 m	mixed agricultural
30	K003	S05-00266	SGMN	Spring	0 m	pasture
31	K004	S05-00267	SGMN	Borehole	30 - 100 m	recreational
32	**K006**	**S05-00269**	**SGMN**	**Borehole**	**30 - 100 m**	**arable**
33	K007	S05-00270	SGMN	Spring	0 m	mixed agricultural
34	K008	S05-00271	SGMN	Spring	0 m	pasture
35	K011	S05-00273	SGMN	Spring	0 m	woodland
36	K012	S05-00275	SGMN	Spring	0 m	pasture
37	K016	S05-00278	SGMN	Borehole	30 - 100 m	semi natural

ID	Field ID	Lab Sample ID	Project	Source type	Depth (m)	Land use
38	K019	S05-00279	SGMN	Borehole	30 - 100 m	pasture DPP
39	K022	S05-00282	SGMN	Borehole	5 - 30 m	pasture
40	S001	S04-01043	Nith 2004	Spring	0 m	semi natural
41	S002	S04-01042	Nith 2004	Spring	0 m	arable
42	S008	S04-01038	Nith 2004	Spring	0 m	pasture DPP
43	S010	S04-01030	Nith 2004	Spring	0 m	pasture
44	S018	S04-01037	Nith 2004	Spring	0 m	pasture
45	SN/107	S02-00231	Original nitrate	Borehole	30 - 100 m	woodland
46	SN/108	S02-00232	Original nitrate	Borehole	30 - 100 m	mixed agricultural
47	SN/110	S02-00233	Original nitrate	Borehole	30 - 100 m	arable
48	SN/111	S02-00234	Original nitrate	Borehole	unknown	pasture
49	SN/114	S02-00235	Original nitrate	Borehole	30 - 100 m	arable
50	SN/115	S02-00236	Original nitrate	Borehole	30 - 100 m	arable
51	SN/116	S02-00237	Original nitrate	Borehole	unknown	mixed agricultural
52	SN/117	S02-00238	Original nitrate	Borehole	unknown	arable
53	SN/118	S02-00239	Original nitrate	Borehole	30 - 100 m	pasture
54	SN/119	S02-00240	Original nitrate	Borehole	30 - 100 m	pasture
55	SN/120	S02-00241	Original nitrate	Borehole	30 - 100 m	mixed agricultural
56	SW001	S06-00753	Baseline SW	Borehole	unknown	pasture DPP
57	SW002	S06-00754	Baseline SW	Borehole	30 - 100 m	pasture DPP
58	**SW003**	**S06-00755**	**Baseline SW**	**Borehole**	**30 - 100 m**	**recreational**
59	SW004	S06-00756	Baseline SW	Borehole	> 100 m	recreational
60	SW005	S06-00757	Baseline SW	Borehole	5 - 30 m	pasture
61	SW006	S06-00758	Baseline SW	Well	< 5 m	pasture
62	**SW007**	**S06-00759**	**Baseline SW**	**Borehole**	**30 - 100 m**	**pasture**
63	SW008	S06-00760	Baseline SW	Borehole	30 - 100 m	pasture
64	SW009	S06-00761	Baseline SW	Spring	< 5 m	pasture
65	SW010	S06-00762	Baseline SW	Borehole	unknown	pasture DPP
66	SW012	S06-00764	Baseline SW	Borehole	0 m	semi natural
67	SW013	S06-00765	Baseline SW	Borehole	30 - 100 m	semi natural
68	SW014	S06-00766	Baseline SW	Borehole	unknown	semi natural
69	SW015	S06-00767	Baseline SW	Spring	0 m	semi natural
70	SW016	S06-00768	Baseline SW	Borehole	30 - 100 m	semi natural
71	SW017	S06-00769	Baseline SW	Borehole	30 - 100 m	pasture
72	SW018	S06-00770	Baseline SW	Spring	0 m	semi natural
73	**SW019**	**S06-00771**	**Baseline SW**	**Borehole**	**30 - 100 m**	**recreational**
74	**SW020**	**S06-00772**	**Baseline SW**	**Borehole**	**30 - 100 m**	**semi natural**
75	SW021	S06-00773	Baseline SW	Borehole	unknown	semi natural
76	SW022	S06-00774	Baseline SW	Borehole	30 - 100 m	mixed agricultural

ID	Field ID	Lab Sample ID	Project	Source type	Depth (m)	Land use
77	SW023	S06-00775	Baseline SW	Spring (min)	0 m	semi natural
78	**WM1**	**S06-00783**	**MHHG_05_08**	**Borehole**	**30 - 100 m**	**mixed agricultural**

The ID number (left hand column) is used to identity samples throughout this report.
The ten selected baseline samples are highlighted in bold.